

Preparation and passivation of GaAs(001) surfaces for growing organic molecules

N Nicoara¹, I Cerrillo², D Xueming¹, J M García³, B García⁴,
C Gómez-Navarro¹, J Méndez^{1,5} and A M Baró¹

¹ Laboratorio de Nuevas Microscopías, Dept Física de la Materia Condensada, Universidad Autónoma de Madrid, 28049, Spain

² Material Physics Laboratory, University of Wales, Aberystwyth, UK

³ Instituto de Microelectrónica de Madrid CSIC, Spain

⁴ Dept Física Aplicada, Universidad Autónoma de Madrid, 28049, Spain

E-mail: javier.mendez@uam.es

Received 21 November 2001, in final form 13 March 2002

Published 23 May 2002

Online at stacks.iop.org/Nano/13/352

Abstract

Growth of ordered organic films of 3, 4, 9, 10-perylene-tetracarboxylic-dianhydride (PTCDA), on inorganic substrates of GaAs(001) is investigated by means of low-energy electron diffraction, scanning tunnelling microscopy and atomic force microscopy. The passivation of the sample can be achieved by exposing the substrate to sulphur (the SnS₂ compound) or wet-chemical etching using an S-containing etchant (S₂Cl₂). The sulphur-treated surfaces are less reactive and are suitable as substrates for the growth of epitaxial films. In this work we have compared the growth of organic molecules on substrates prepared by two different methods. The samples prepared by molecular beam epitaxy (MBE) present smoother surfaces compared with chemically treated samples. Therefore, an improvement of the PTCDA molecular order is observed for the MBE samples, which exhibit the formation of crystals.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Growth of vacuum-deposited thin films on inorganic semiconductors has received considerable interest in the last few years in view of possible applications of these materials in optoelectronic devices. The passivation of inorganic semiconductors was found to improve the growth of organic molecular films [1]. Semiconductors present a high density of states at the surface, caused by chemically active defects such as dangling bonds, steps and vacancies [2]. These surface states affect the molecular ordering of the organic films. Many attempts have been made to reduce the reactivity of the substrate [1, 3] and subsequently the strength of the interaction between the film and substrate. The purpose of passivation is to obtain chemically and electronically passivated surfaces.

Several methods have been developed for passivation of GaAs(100) surfaces [4–6]. In this work we used a sulphur passivation method, which has recently received attention due

to the improvement of device performance that it achieves. The passivation can be achieved by immersing GaAs samples in a sulphur solution such as S₂Cl₂ [7]. It has been pointed out that this removes the native oxide of GaAs and forms a S-terminated layer. The passivated substrates are characterized by means of low-energy electron diffraction (LEED), scanning tunnelling microscopy (STM) and atomic force microscopy (AFM). As we show in this work, one inconvenience inherent to *ex situ* chemical treatment is that it provides rough surfaces, which are not appropriate for growing ordered organic layers. It is known that the preparation of a well ordered and clean sample of a III–V compound usually requires molecular beam epitaxy (MBE) techniques or *ex situ* MBE together with arsenic cap protection.

The organic molecule perylene-tetracarboxylic-dianhydride (PTCDA) presents quasiepitaxial growth on different substrates [8]. The ordering of the first layer is decisive for the entire epitaxial growth. The mechanism controlling the adsorption of large molecules on the surfaces is not well known.

⁵ Author to whom any correspondence should be addressed.

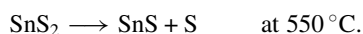
From STM and AFM topographic images, we obtain information about the nucleation and growth of deposited PTCDA. We compare substrates prepared by two different methods and the growth of the organic layers on these substrates.

2. Experimental procedure

Experiments were performed in an ultrahigh-vacuum (UHV) system, consisting of load-lock, analysis and STM chambers, with a base pressure of 1×10^{-10} Torr. The STM is a beetle-type instrument using W tips. We used GaAs(001) epitaxial wafers, n-doped to $1\text{--}4 \times 10^{18} \text{ cm}^{-3}$.

Two different methods were performed in order to obtain passivated substrates. The first method involves an *ex situ* chemical treatment. Samples were chemically cleaned in an ultrasonic bath with acetone, ethanol and de-ionized water for 5 min each and dried in flowing nitrogen. After degreasing, the samples are dipped in $\text{S}_2\text{Cl}_2:\text{CCl}_4 = 1:3$ solution for 15 s. The effect of the etching is to remove the native oxide and to form S-terminated surfaces. To remove the residual S_2Cl_2 on the surface, the sample was rinsed in CCl_4 (5 s), acetone, ethanol and de-ionized water [7]. The CCl_4 rinse, which follows the etching, plays an important role in avoiding the reaction of S_2Cl_2 with water molecules, which will result in failure of passivation. The sample was then loaded into the UHV system. Prior to growth of the PTCDA organic films, the sample was annealed for 20 min at 450°C in order to remove the residual sulphur and other contaminants. (2×1) LEED patterns, characteristic for the passivated GaAs(001) surfaces, are observed.

For comparison we have used a second method. In this, samples are regrown in a separate solid-source MBE system. An epitaxial GaAs layer of 180 nm, silicon doped ($1 \times 10^{18} \text{ cm}^{-3}$), was grown to flatten the surface. Then, an amorphous As_2 layer was deposited at room temperature to avoid surface oxidation during exposure to air [9, 10]. The sample was then transferred to the ultrahigh-vacuum system where the experiments are performed. After thermal desorption of the As cap at 450°C for 45 min, the LEED pattern shows an As-terminated (2×4) surface reconstruction. The substrate kept at room temperature is then passivated by exposing to S (evaporated from a SnS_2 compound) [11]. A quadrupolar mass spectrometer was used to examine the desorbate composition as a function of source temperature. It is known that this compound decomposes at high temperatures [12]:



After sulphur deposition the sample was then annealed for 10 min at 450°C to smooth the resulting surface.

Deposition of PTCDA is achieved by molecular organic vapour deposition (MOVD), using an evaporator containing the organic material. In order to remove possible impurities from the organic material, the evaporator was held for several hours at lower temperature than the specific sublimation temperature of PTCDA, before the effective evaporation was started.

AFM and STM analysis were performed in order to obtain information about the substrate and the growth of organic material on these samples.

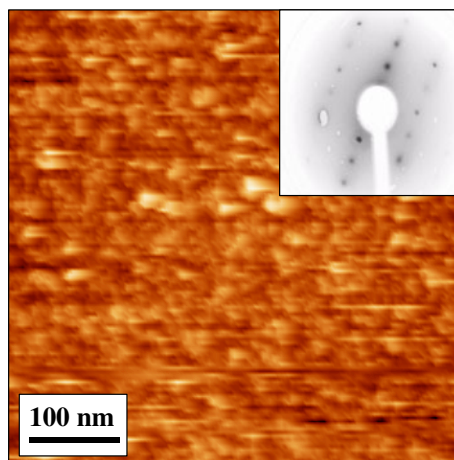


Figure 1. A STM image ($500 \text{ nm} \times 500 \text{ nm}$) showing the sulphur-passivated GaAs(001) substrate before PTCDA deposition. The sample has been chemically prepared with a $\text{S}_2\text{Cl}_2 + \text{CCl}_4$ solution. The inset shows a (2×1) LEED pattern obtained for this sample at 82 eV.

3. Results and discussion

We have investigated by means of LEED, AFM and STM the structure and the roughness of GaAs(001) surfaces prepared by two different methods and the growth of PTCDA on these substrates. We compare the results obtained for the two methods and the resulting organic layers deposited on these surfaces.

3.1. Chemically treated samples

For the chemical treatment by etching of the samples in S_2Cl_2 solution described above, the parameters of the etching solution were changed. Best results are observed after 15 s etching in $\text{S}_2\text{Cl}_2:\text{CCl}_4 = 1:3$. The LEED pattern is shown in the inset of figure 1. While the (2×1) GaAs surface reconstruction is clear from the LEED results, investigation of the samples using STM (in figure 1) does not reveal any surface reconstruction. To explain the fact that we observe a LEED pattern from these surfaces while STM does not show an ordered structure, we have to consider that the LEED technique integrates over the area of the spot size ($\sim 1 \text{ mm}^2$). To observe a LEED pattern, only 30% of the sample has to be ordered. In contrast, STM requires at least 70% of the surface to be ordered to obtain a reasonable image. Roughness analysis measuring the root mean square (RMS) from STM images gives values close to 0.66 nm (for $250 \text{ nm} \times 250 \text{ nm}$ images). From these results we deduce that the chemically treated samples are rough. It is known that the etching could affect the uniformity of the sample surface.

In order to study the growth of organic material, PTCDA is evaporated on these substrates. After vapour deposition of the molecules at room temperature on the chemically treated samples, no ordered organic layers of PTCDA are observed in the STM images. As can be seen in figure 2, the deposition leads to the formation of non-ordered aggregates. From this work, we cannot distinguish whether these PTCDA aggregates are crystals with random orientation or if they are non-crystalline on these substrates. We can only point out that

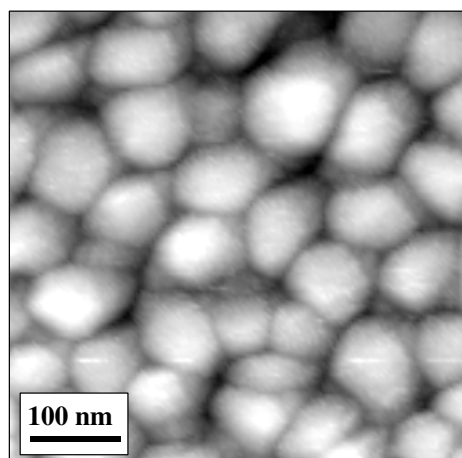


Figure 2. A STM image ($500 \text{ nm} \times 500 \text{ nm}$) after deposition of PTCDA on the chemically prepared substrate. The organic molecules grown at room temperature form non-ordered aggregates. No order has been observed under these deposition conditions.

the organic layers formed on the chemically prepared samples present no facets which would clearly indicate crystalline nature.

3.2. MBE-prepared samples

After removing the As cap of the MBE-prepared samples, we observed the (2×4) LEED pattern characteristic of reconstructed As-rich GaAs(001) surfaces. Further characterization of the samples using STM shows rows along the $[\bar{1}10]$ direction, corresponding to the dimer rows of the (2×4) reconstruction. This can be observed in figure 3, where an image obtained at a negative bias of -2.5 V and a tunnelling current of 1.5 nA is depicted. In agreement with other authors [13], we found that stable tunnelling could be achieved only at negative bias of the sample with respect to the tip. At the opposite polarity, tunnelling is unstable and it was almost impossible to obtain images. This could be explained by the fact that, when applying negative bias, electrons come from filled states in the sample, which are expected to be concentrated in arsenic. Consistently with this, we consider that at this surface we have arsenic, as expected for a (2×4) reconstruction. Also, it can be noted that most of the image presents regions on several terraces with ordered (2×4) structure. The brighter areas, apparently not ordered, also appear elongated along the $[\bar{1}10]$ direction. With the same argument as was used before, these areas could be assigned to arsenic on the topmost layer. In the inset of the figure, a higher-magnification image resolves the dimers inside the rows. The unit cell of the (2×4) reconstruction has been marked, as have the dimers corresponding to the model proposed by Chadi [14] and confirmed as the most stable structure for this surface [15].

Following the passivation by evaporation of sulphur from the SnS_2 compound, and after removing the sulphur excess, PTCDA was evaporated onto these MBE samples at room temperature. It is known that the passivation process improves the growth of the organic molecules, reducing the density of states at the surface. Force and tunnelling microscopy results show that the organic molecules form aggregates, similar to the ones on the chemically prepared samples. The difference

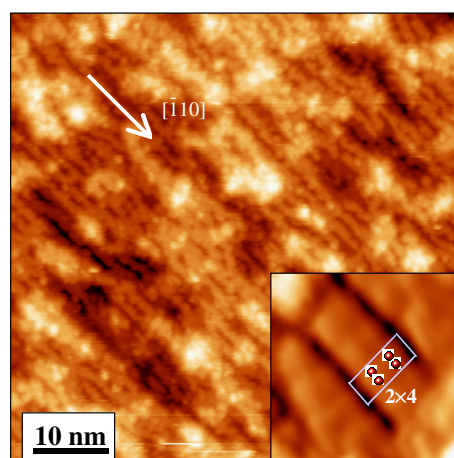


Figure 3. A STM image obtained for the MBE-prepared GaAs(001) substrate after removing the As cap at 500°C . The dimensions are $60 \text{ nm} \times 60 \text{ nm}$ and 1.4 nm for the vertical scale. The surface presents areas with rows of dimers corresponding to the (2×4) reconstruction of the As-rich GaAs(001). Dimers can be resolved as observed in the inset ($4.7 \text{ nm} \times 4.7 \text{ nm}$). The RMS roughness value (0.22 nm) obtained for this preparation is much lower than that for the chemical treatment (0.38 nm).

in this case is that some of them present facets, indicative of the formation of crystals. In figure 4, an AFM image shows this crystalline growth. The image is represented in derivative mode for a better visualization. In the lower part of the image, several crystals of PTCDA are observed, with facets and steps clearly corresponding to an ordered growth. On closer inspection of these crystals, domains of organic molecules are observed by STM (not presented here). Figure 5 shows a current STM image of the ordered molecules of PTCDA in one of these domains. The PTCDA unit-cell values measured ($1.2 \text{ nm} \times 2.0 \text{ nm}$) are in good agreement with the bulk PTCDA distances ($1.19 \text{ nm} \times 1.99 \text{ nm}$) [1, 16]. In the image, individual molecules with the same orientation can be observed along the diagonal indicated by the arrow. The next rows appear rotated, as is typical for the PTCDA structure. Other authors have identified this structure on different substrates [8] and the internal structure of individual molecules, observed in the STM images, has been correlated with molecular orbital calculations for the PTCDA molecule [17].

3.3. Comparison of the two preparation methods

As mentioned above, the STM images of the GaAs(001) substrates for the two preparation methods exhibit substantial differences. For the chemically prepared samples, the reconstruction is not observed and the surface is rough, as can be deduced from the RMS analysis (see table 1). In contrast, for the MBE case, the sample presents surface reconstruction and the roughness values are much smaller (0.27 nm for the MBE-prepared sample against 0.66 nm for the chemically prepared sample, for the same image sizes and similar annealing temperatures). In table 1, a comparison of the roughness values for the two methods is presented. The difference between the chemically treated sample and the others obtained by MBE is evident. In order to avoid local effects, RMS roughness

Table 1. RMS roughness analysis from STM.

S-passivated GaAs(001), chemical preparation, RMS (nm)		GaAs(001), MBE preparation, RMS (nm)		Annealing temperature (°C)
50 nm × 50 nm	250 nm × 250 nm	50 nm × 50 nm	250 nm × 250 nm	
0.38	0.66	0.21 0.22 0.11	0.39 0.27 0.19	$T = 450$ $T = 500$ $T = 550$
PTCDA on S-passivated GaAs(001), chemical preparation, RMS (nm)		PTCDA on S-passivated GaAs(001), MBE preparation, RMS (nm)		
50 nm × 50 nm	500 nm × 500 nm	50 nm × 50 nm	500 nm × 500 nm	
0.56	1.06	0.53	1.49	

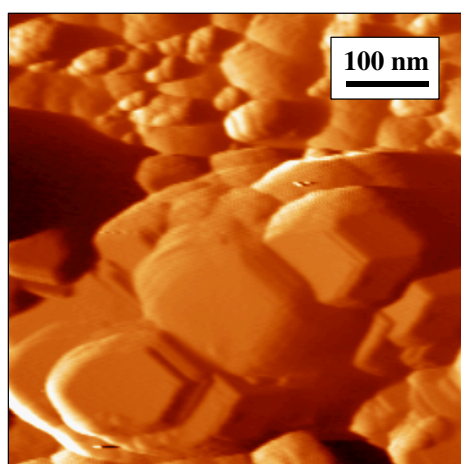


Figure 4. A derivative AFM image (550 nm × 550 nm) showing PTCDA deposited on a MBE-prepared sample. The organic material presents terraces where molecular resolution has been achieved. The height at the highest point is close to 100 nm with respect to the GaAs substrate, corresponding to several hundreds of organic layers.

analysis has been performed on different areas and using different image sizes. For the MBE-prepared samples, an analysis for different preparation temperatures was also made in order to investigate the dependence of the roughness on the annealing conditions. It can be observed that the roughness values become smaller as the temperature of the annealing is increased.

After deposition of PTCDA on the two substrates, ordering of the organic layer was only obtained for the MBE-prepared samples. An appropriate substrate preparation, such as that for the *ex situ* MBE-prepared samples, has a decisive influence on the morphology of the organic layer grown on it. This is a fact relevant to the performance of devices based on organic thin films.

Further investigation of the electronic transport through the substrate, for both preparation methods, and the adsorbed organic molecules is presented elsewhere [18].

4. Conclusions

We have compared two different preparation methods for sulphur passivation of GaAs(001) surfaces. How these methods affect the substrates and consequently the growth of

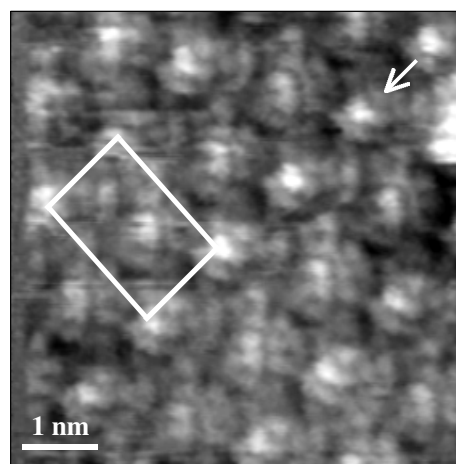


Figure 5. A STM current image (5.9 nm × 5.9 nm) of PTCDA on GaAs(001) showing a unit cell consisting of two molecules. The marked cell is 1.2 nm × 2.0 nm, which corresponds to the bulk PTCDA distances (1.19 nm × 1.99 nm). The arrow indicates the direction in which the organic molecules have the same orientation. $I = 3.15$ nA, $V = -3.6$ V.

PTCDA has been analysed by means of LEED, STM and AFM. From STM data, no reconstruction of the surface and no order of the organic layer is observed for the chemically prepared samples. On the other hand, MBE-prepared samples exhibit reconstruction of the surface and molecular order of the organic layer, as is shown in the STM images. The morphology of the PTCDA organic layer grown on GaAs(001) depends on the roughness of the inorganic semiconductor substrate and, therefore, on the preparation method.

Acknowledgments

Funding for this work was provided by EU Network DIODE (contract no: HPRN-CT-1999-00164). JMG also acknowledges financial funding from Comunidad Autónoma de Madrid, 07T/0062/2000. NN and IC are grateful for DIODE European grants. The authors acknowledge Óscar Custance for STM design and J Gómez-Herrero and J M Gómez-Rodríguez for critical readings.

References

- [1] Kendrick C and Kahn A 1998 *Surf. Rev. Lett.* **5** 289
- [2] Sandroff C J, Nottenburg R N, Bischoff J-C and Bhat R 1987 *Appl. Phys. Lett.* **51** 33
- [3] Sandroff C J, Hegde M S, Farrow L A, Bhat R, Harbison J P and Chang C C 1990 *J. Appl. Phys.* **67** 586
- [4] Spindt C J, Liu D, Miyano K, Meissner P L, Chiang T T, Kendelewicz T, Lindau I and Spicer W E 1989 *Appl. Phys. Lett.* **55** 861
- [5] Hou X Y, Cai W Z, He Z Q, Hao P H, Li Z S, Ding X M and Wang X 1992 *Appl. Phys. Lett.* **60** 2252
- [6] Hou X Y, Chen Y, Li Z S, Ding X M and Wang X 1996 *Appl. Phys. Lett.* **69** 1429
- [7] Li Z S, Cai W Z, Su R Z, Dong G S, Huang D M, Ding X M, Hou X Y and Wang X 1994 *Appl. Phys. Lett.* **64** 3425
- [8] Forrest S R 1997 *Chem. Rev.* **97** 1793
- [9] Boubeta C M *et al* 2001 *Surf. Sci.* **482** 910
- [10] Jackson M D, Thornton J M C, Woolf D A and Weightman P 1996 *Surf. Sci.* **352-4** 724
- [11] Zahn D R T, Kampen T U, Hohenecker S and Braun W 2000 *Vacuum* **57** 139
- [12] Shimada T, Ohuchi F S and Parkinson B A 1992 *J. Vac. Sci. Technol. A* **10** 539
- [13] Pashley M D, Haberern K W, Friday W, Woodall J M and Kirchner P D 1998 *Phys. Rev. Lett.* **60** 2176
- [14] Chadi D J 1987 *J. Vac. Sci. Technol. A* **5** 834
- [15] Xue Q-K, Hashizume T and Sakurai T 1999 *Appl. Surf. Sci.* **141** 244
- [16] Hirose Y, Forrest S R and Kahn A 1995 *Appl. Phys. Lett.* **66** 944
- [17] Kendrick C, Kahn A and Forrest S R 1996 *Appl. Surf. Sci.* **104-5** 586
- [18] Méndez J, Nicoara N, Cerrillo I, Custance O and Baró A M 2002 *Nanotechnology* submitted