Title: Low temperature oxide desorption in GaAs (111)A substrates

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Abstract

The aim of this work is to study oxide removal processes on GaAs (111) A substrates previous to epitaxial growth. We have studied conventional thermal desorption and processes based on the reduction of surface oxides by deposition of gallium, indium and exposure to atomic hydrogen.

We have determined substrate temperatures (T_s) for optimum oxide removal in epi-ready substrates by the different studied processes: T_s= 540 ºC for thermal desorption, T_s= 505ºC for indium deposition and Ts = 400º C for oxide desorption by exposure to atomic hydrogen. All these processes allow for a subsequent good quality epitaxial growth. These results cannot be directly extended to oxide removal in grown samples that have been exposed to air outside the growth chamber. In this case, we have found that only indium deposition and exposure to atomic hydrogen are compatible with regrowth processes.

Keywords:

Molecular beam epitaxy; Gallium Arsenide

1. Introduction

Quantum dots (QD) grown on GaAs(111) substrates are highly potential for entangled photon devices based on the cascade relaxation of biexcitons, as they present a fine structure splitting close to zero [1-3]. For that purpose it is desirable to control the density, the emission energy and the position of the QD. Particularly, control of the position of QD often involves regrowth steps on previously fabricated patterned substrates [4-6]. The patterning is commonly carried out on epitaxial substrates, i.e. substrates where an epitaxial layer has already been grown. Consequently, during the patterning processes previous to regrowth, the epitaxial substrates are exposed to air without any passivizing layer (as the commercial epi-ready substrates have). Moreover, the oxides formed at the patterned epitaxial substrates have to be removed before regrowth at low enough temperature processes for preserving patterned motifs. All these requirements, common to any substrate orientation, are specially demanding in case of GaAs(111) substrates, where even homoepitaxial growth can be considered a challenge. Furthermore, in case of GaAs(111)A orientation, no precise determination has been reported in the literature in relation with the oxide removal previous to epitaxial growth even for the most conventional procedure, the thermal desorption at high substrate temperature.

The aim of this work is to study oxide removal in GaAs(111)A substrates with special emphasis in those processes that permit to decrease the maximum substrate temperature leaving a surface morphology that can be eventually flattened after the growth of a few nanometers of GaAs. Besides conventional thermal desorption, the processes under study are based on the reduction of surface oxides, particularly Ga_2O_3 to produce other oxides that are volatile at lower temperatures [7-12]. In this way, we exposed the GaAs(111)A surfaces to Ga, In and atomic hydrogen beams. We will also show the differences observed in the oxide desorption process between epitaxial and epi-ready substrates. Our results demonstrate that the substrate temperature necessary for oxide thermal desorption in GaAs (111)A epi-ready substrates is significantly lower than that in GaAs(001) substrates (T_s=580ºC in our system). However, in the case of GaAs(111)A epitaxial substrates, it is necessary to increase the substrate temperature up to 600ºC to remove oxides, process that results in a strong degradation of surface morphology. Instead we propose for GaAs(111)A epitaxial substrates to remove oxides by In deposition at T_s=525ºC. This process seems to be very promising for application in regrowth procedures on patterned substrates.

2. Experiment description

The substrates used in this work were GaAs(111)A In-bonding to a holder. Previously to the introduction in the growth chamber, they were heated to 250 ºC for 20 min in the pre chamber of a RIBER Compact 21E molecular beam epitaxy (MBE) system. Substrate temperature (T_s) was measured using an optical pyrometer assuming that the transition temperature of the surface reconstruction from (2x4) to c(4x4) under an As_4 flux equivalent to 2 monolayers per second (ML/s) on a GaAs(001) surface is 520 ºC [13]. The oxide desorption was *in situ* monitored by recording the evolution of the intensity of the reflection high energy electron diffraction (RHEED) specular beam, I_{00}, in a <112> azimuth during the oxide desorption process. *Ex situ* morphology characterization, after the different processes undertaken for the oxide removal, was performed by atomic force microscopy (AFM) using a commercial Nanotec scanning probe microscopy system and silicon tips (K= 40 N/m and radius < 10 nm) in dynamic mode.

We have studied the oxide desorption process on two types of semi-insulating GaAs(111)A substrates: commercially available epi-ready and epitaxial substrates. The epitaxial substrates consist of 135 nm of GaAs grown at T_s=525 ºC. A Ga growth rate of 0.2 ML/s and an As_4 flux equivalent to 7 ML/s were employed. Once grown, the epitaxial substrates were air exposed and detached from the holder by heating at temperatures slightly higher than the In melting point (156 ºC). They are maintained under N_2 atmosphere during two months until they are In bonding again to a new holder for their use as substrates for further epitaxial growth. Notice that during substrate detachment from the holder and storage before regrowth, a surface GaAs oxide layer starts to form whose composition and thickness will depend on the particular history of each epitaxial substrate piece.

Once epi-ready and epitaxial GaAs (111)A substrates are In bonding to a holder, they are introduced at the MBE load-lock chamber and grown within a time period of 24 hours.

For thermal desorption we followed two ways. In the first one, we made a similar process to that conventionally used on GaAs (001) substrates; T_s was increased at 15ºC / min at T_s= 600 ºC (20 ºC above T_s for oxide desorption in our experimental setup) under an As_4 flux equivalent to 2 ML/s (As_4 cell was opened at T_s=520ºC) and it is maintained at this temperature during 5 minutes. The second process consisted of increasing T_s very slowly in order to identify the lowest temperature at which the oxide is removed. In particular, T_s was increased in steps of 6 ºC from 530 ºC with a dwell time of 20 min. Once the minimum T_s for oxide desorption was detected, the temperature was increase 20ºC over this value during 5 minutes.

Oxide removal by Ga/In deposition was studied for T_s > 500 ºC, substrate temperatures above the In_2O or Ga_2O desorption temperature [14, 15]. Two different T_s (400 ºC and 490ºC) were explored for oxide removal by exposure to an atomic hydrogen beam, both of them above Ga_2O desorption onset temperature (350ºC-400ºC) [15].

For Ga/In deposition, the III-element deposition rate was 0.01 (ML/s) (measured in GaAs(001) substrates).The experiments were made at T_s= 520, 540 and 560ºC for Ga deposition and Ts= 505, 520 and 540 ºC for In deposition. For the oxide removal by exposure to an atomic hydrogen beam, a H_2 base pressure of 1.33×10^{-3} Pa during 10 minutes was used and two different substrate temperature, T_s= 400 ºC and T_s= 490 ºC.

Finally, in order to check the evolution of the surface morphology after the different oxide removal processes under study, samples consisting of a 5 nm thick GaAs layer grown at 0.2 ML/s and an As flux equivalent to 7ML/s were fabricated on GaAs(111)A for AFM characterization.

After the different processes were finished, samples were immediately cooled down and taken out from the MBE system for AFM measurements.

3. Results and discussion

Taking into account that our maximum interest is focused to regrowth of patterned epitaxial substrates, it will be imperative to detect the differences in the oxide desorption process between epitaxial and epi-ready substrates. We have to take into account that neither thickness nor composition of the oxide layer is identical in epitaxial and epi-ready substrates. It is expectable that epitaxial substrates have a thicker oxide layer with higher Ga_2O_3 content [16] than epi-ready ones, considering that epitaxial substrates have undergone In bonding and detachment processes (without any special passivation oxide layer) and have been out of vacuum for two months.

First, we discuss the thermal desorption results comparing epi-ready and epitaxial substrates. Our results show that thermal oxide desorption from the surface of an epi-ready GaAs(111)A substrate, as detected when the I_{00} intensity reaches a maximum at the RHEED pattern observed in <112> azimuth, takes place at T_s=540 ºC. This substrate temperature is lower than that typically observed in our MBE system for GaAs (001) substrates (T_s=580ºC). Fig. 1 shows the AFM images corresponding to GaAs (111)A surface after oxide desorption at 540ºC and heated at 560ºC during 5 min. (a) and at 580ºC and heated at 600ºC during 5 min (b). A flat surface with pits can be observed following both procedures. An increase of T_s up to 600ºC (as in GaAs (001) substrates oxide thermal desorption) results in a surface with lower density but deeper pits (see the AFM profiles shown on bottom part of Fig. 1).

On the contrary, in case of a GaAs (111)A epitaxial substrate, we have observed that heating the sample up to 540 ºC is not enough even to observe the appearance of a RHEED pattern. It is necessary to increase T_s up to 600 ºC to obtain a faint RHEED diagram. As we will show later, the GaAs(111)A surface obtained with this procedure is not compatible with a subsequent good epitaxial growth.

GaAs(111)A surface oxide desorption by using Ga or In deposition has been monitored in real time trough the evolution of I_{00} RHEED intensity in <112> azimuth.

Fig. 2(a) shows I_{00}, normalized to the maximum signal, as a function of Ga deposition (in equivalent of GaAs (001) monolayers) obtained in GaAs epi-ready substrates for different substrate temperatures. We observe a similar I_{00} evolution at any T_s under study: a rise of I_{00} intensity followed by a decay, showing a clear maximum for a certain amount of Ga deposited. The increase of RHEED intensity in the first stage is due to the substrate oxides reduction and subsequent desorption, reaching an I_{00} intensity maximum value when this oxide layer is completely removed, as previously observed in GaAs (001) substrates [7, 8]. Further Ga deposition leads to a decrease of I_{00} in coincidence with Ga droplet formation on the surface. We also observe that the amount of Ga deposited for reaching the I_{00} intensity maximum depends on T_s. The lower the substrate temperature, the larger the amount of Ga required*:* 5.2, 3.7 and 3.0 ML for T_s = 520, 540 and 560 ºC respectively.

Fig. 2(b) shows the AFM image of GaAs (111)A epi-ready substrate on which the oxide desorption process took place at T_S= 520 ºC by depositing 8 ML of Ga (2.8 ML in excess to that required for oxide removal according to the maximum of I_{00} RHEED signal). We observe a flat surface with a high density of shallow pits, together with the formation of Ga droplets. These results show that the oxides desorption by Ga deposition is highly risky, as it is necessary a sub-monolayer control of the amount deposited in order to avoid droplet formation. From the Arrhenius plot of the inverse of the amount of Ga needed to fully remove the surface oxide versus T_S [11] we obtain an activation energy of 0.9 eV, related to the different processes occurring on the surface (Ga diffusion towards oxidized areas, Ga-oxide reduction, oxide desorption, etc.).

We have extended the previous work to In deposition. Fig. 3(a) shows I_{00} RHEED intensity as a function of In monolayers deposited at different substrate temperatures. As in the case of oxide removal by Ga, we observe an I_{00} rise up with In deposition. Similarly, the amount of In necessary to reach I_{00} maximum decreases for increasing substrate temperature: 8.9, 5.3 and 2.6 ML for T_s= 505, 520 and 540 ºC respectively. As a difference with the above shown results using Ga (Fig. 2(a)), I_{00} remains constant after reaching a maximum intensity, except for the lower T_s (505 ºC), where we observe that I_{00} decreases after the I_{00} saturation value has been reached. Oversupplied In at Ts= 520 and 540 ºC temperatures does not cause change in I_{00} intensity. This means that once oxide has been removed, evaporation of excess of In takes place. However, at the lowest substrate temperature studied, 505 ºC, the decrease in I_{00} indicates that In surface evaporation is not as efficient as at higher T_s, and droplet appears at the surface due to In excess. Anyway, this is not a serious problem, as In droplets can be easily evaporated just by a small increase of substrate temperature. Thus, a sub-monolayer precision in III element deposition is not needed for surface oxides removal when In is the supplying element. The AFM image on Fig. 3b shows that, in spite of the large amount of excess of In (9.7 ML of In in excess to that required for oxide removal at T_S= 520 ºC), no In droplets appear on the surface. Otherwise, the surface morphology is similar to that observed for Ga deposition (Fig 2b), showing a high density of shallow pits.

The Arrhenius plot of the inverse of amount of In deposited to reach the maximum of I_{00} versus T_s permits to obtain an activation energy of 1.8 eV, very similar to 1.90 eV previously reported in the literature for GaAs(001) substrates [11]. The higher activation energy for the oxide desorption process in the case of In deposition as compared with Ga (0.9 eV) indicates that the oxide removal process by In is less efficient than by Ga.

So, from these results we have established that In deposition is a convenient process to remove surface oxides in GaAs(111)A epi-ready substrates at a substrate temperature Ts= 520ºC (20 ºC below the temperature for oxide removal by thermal treatment).

However, our maximum interest is focused to patterned epitaxial substrates, as oxide thermal desorption processes imply high substrate temperatures smoothing the patterned motifs and leading to rough surfaces not compatible with further selective epitaxial growth. For evaluating the oxide desorption process by In supplying on epitaxial substrates we have deposited In at T_s=520 ºC, as its excess does not lead to In droplet formation. Fig.4 shows the I_{00} RHEED intensity evolution as a function of the amount of In deposited at T_s= 520 ºC (all plots have been normalized at the I_{00} saturation value) for an epi-ready and an epitaxial substrate. As previously shown (Fig. 3(a)), we observe an initial I_{00} increase corresponding to the removal process of the oxide layer, followed by a saturation value, in coincidence with the oxide removal. However, 12.9 ML monolayers are needed to achieve a steady value of I_{00} for the epitaxial substrates, a much larger amount than the 5.3 ML of In necessary to remove the oxide in an epi-ready substrate at this T_s. In this way, the amount of In necessary for a complete removal of the oxide layer is larger for epitaxial substrates than for epi-ready ones. This is not surprising, because in the epitaxial substrates employed in this work, a thicker oxide layer with higher Ga_2O_3 content [16] is expectable as we mentioned before.

With the same aim of decrease substrate temperature for oxide desorption, we have also studied GaAs (111)A oxide removal process by reducing surface oxides with atomic hydrogen besides deposition of Ga and In. This process has been revealed as a powerful process in terms of low substrate temperature and resulting surface morphology [12]. We have implemented this process at substrate temperatures T_s= 400 C and 490 C for epi-ready GaAs(111)A samples. On Fig. 5 we show an AFM image of both samples. The morphology of the substrate kept at Ts= 400 ºC under a hydrogen beam shows a dramatic improvement respect to the previous experiments. On the other hand, the substrate kept at T_s = 490 ºC under hydrogen exposure shows a totally similar morphology to that of the samples subjected to oxide removal using Ga (see Fig. 2(b)) or In (see Fig. 3(b)) at slightly higher (T_s=520 C) temperature.

Our results show that shallow pits are observed in all the samples after oxide removal, no matter how oxides were removed, except when T_s was maintained as low as 400 ºC. This result point out that the pits are related to Ga oxides reduction processes involving Ga and As from the substrate; these processes are thermally activated, and practically inoperative at T_s= 400ºC.

Finally, we have grown a 5nm thick GaAs layer on epi-ready and epitaxial GaAs(111)A substrates that have undertaken different processes for oxide removal before epitaxial growth. Fig. 6 shows AFM images of the morphology of the 5 nm thick GaAs layer obtained when the oxide desorption is made through In deposition for an epi-ready substrate (a) and for an epitaxial substrate (b). Fig. 6(c) corresponds to the morphology obtained on epitaxial substrate after oxide thermal desorption at 600 ºC. AFM measurements clearly show that 5 nm of GaAs is enough to achieve a flat surface at the atomic step level in epi-ready substrates. In the case of epitaxial substrates it would be desirable to increase the thickness of the GaAs layer to improve morphology. However, a highly rough surface is obtained after growth of 5 nm of GaAs on the epitaxial substrate after oxide removal by thermal treatment, indicating that thermal oxide desorption is not compatible with regrowth processes on epitaxial substrates.

4. Summary and conclusions

We have studied different processes for oxide removal before epitaxial growth on GaAs(111)A epi-ready and epitaxial substrates: oxide removal by thermal desorption and processes based on the reduction of surface oxides by exposing to Ga, In and atomic hydrogen fluxes. We have studied the surface morphology resulting from the different processes.

We have obtained that oxide removal by thermal desorption is achieved at Ts= 540 ºC, well below the temperature required for GaAs (001) substrates (typically 580 ºC).

In the case of oxide removal by depositing a few monolayers of III element, we have observed that deposition of In permit to decrease the substrate temperature to 505 ºC without the formation of metallic droplets until a great excess (more than 6 monolayer) of In has been deposited. In the case of Ga deposition, droplets are formed at any temperature below at least 560 ºC, unless the exact amount of Ga for oxide removal is accurately deposited. This is an important drawback of this process because *a priori* one cannot know the exact amount of Ga necessary for getting a complete surface oxide removal (strongly dependent on the history of each substrate with an oxide layer with specific thickness and composition).

We have studied the surface morphology resulting after the different processes for oxide removal under study. We observe shallow pits, except for the case of oxide reduction by atomic hydrogen at Ts= 400ºC. These results point out that thermal activated processes during oxide removal, not relevant at Ts= 400 ºC, are responsible for the pits formation.

In conclusion, we have studied different oxide removal processes previous to epitaxial growth in GaAs(111) A substrates. We have determined substrate temperatures for optimum oxide removal in epi-ready substrates by the different studied processes: Ts= 540 ºC for thermal desorption, Ts= 505ºC for In deposition and Ts = 400 C for oxide desorption by exposure to atomic hydrogen. All these process allow for a subsequent good quality epitaxial growth. On the contrary, when epitaxial substrates are employed, a slight high temperature (Ts= 525ºC) is needed for oxide removal by In deposition while oxide thermal desorption is not compatible with further epitaxial growth. Both In deposition and exposure to atomic hydrogen have revealed as processes compatible with regrowth in patterned epitaxial substrates.

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Figure Captions

Fig. 1. 4x4 μm^2 AFM image of the GaAs(111)A surface after oxide removal by thermal desorption at a) substrate temperature Ts= 540 ºC and b) Ts= 580 ºC. Profiles marked on the AFM images evidence that the increase in surface temperature produces a surface with a lower density of deeper pits.

Fig. 2. (a) Normalized specular beam RHEED intensity (I_{00}) as a function of Ga monolayers (ML) deposited at substrate temperature Ts = 520, 540, 560 ºC. (b) 4x4 μm^2 AFM image of the GaAs(111)A surface after oxide removal by depositing 8 ML of Ga at Ts= 520ºC.

Fig. 3.(a) Normalized specular beam RHEED intensity (I_{00}) as a function of In monolayers (ML) deposited at substrate temperature T_s= 505, 520, 540 ºC. (b) 4x4 μm^2 AFM image of the GaAs(111)A surfaces after oxide removal by depositing 15 ML of In at T_s = 520 ºC.

Fig. 4. Normalized specular beam RHEED intensity I_{00} as a function of In monolayers (ML) deposited at substrate temperature T_s = 520 ºC for an epi-ready and an epitaxial substrates.

Fig. 5. 4x4 μm^2 AFM image of the GaAs (111) A surface after oxide removal by exposure to atomic hydrogen at a) substrate temperature T_s= 400ºC and b) T_s= 490 ºC. Profiles marked on the AFM images evidence the absence of pitting in the sample treated at Ts= 400 ºC.

Fig. 6. 4x4 μm2 AFM image of the GaAs (111) A surface after the growth of 5 nm thick GaAs layer after a) oxide removal by In from an epi-ready substrate, b) oxide removal by In from an epitaxial substrate and c) thermal oxide desorption from an epitaxial substrate. Observe the drastic improvement of GaAs layer morphology on the epitaxial substrate where oxide was removed by In deposition as compared with oxide removal by thermal desorption.

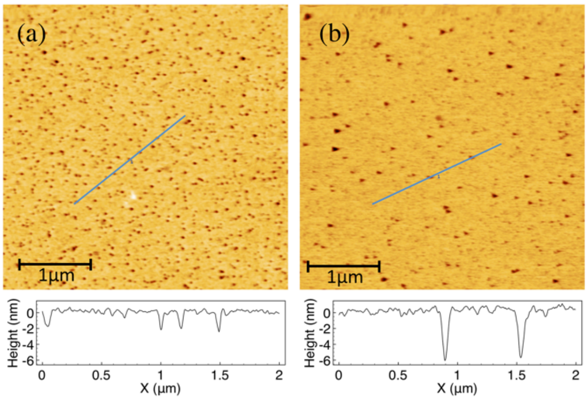
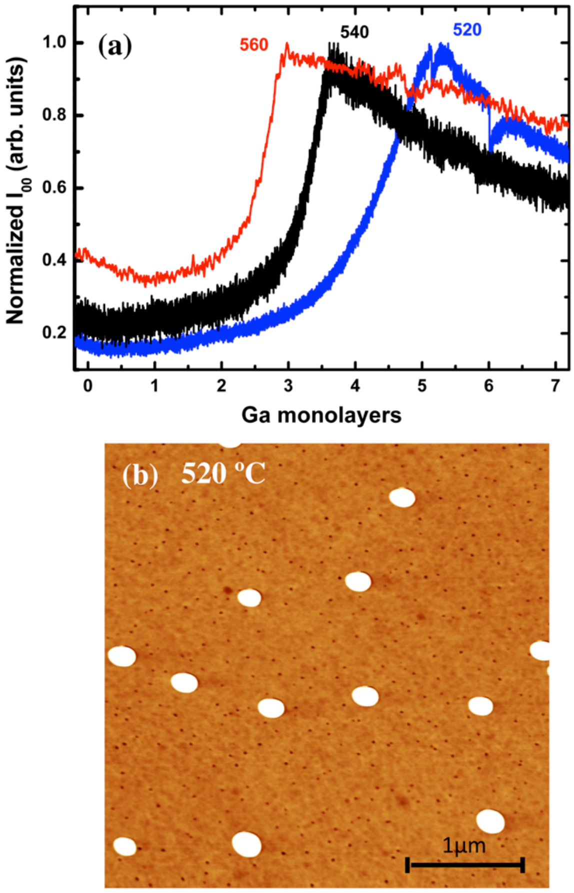

(a)
(b)
1µm
1µm
Height (nm)
0
-2
-4
-6
0
0.5
1
1.5
2
X (µm)

Fig 1.


(a)
560
540
520
Normalized I₀₀ (arb. units)
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0.8
0.6
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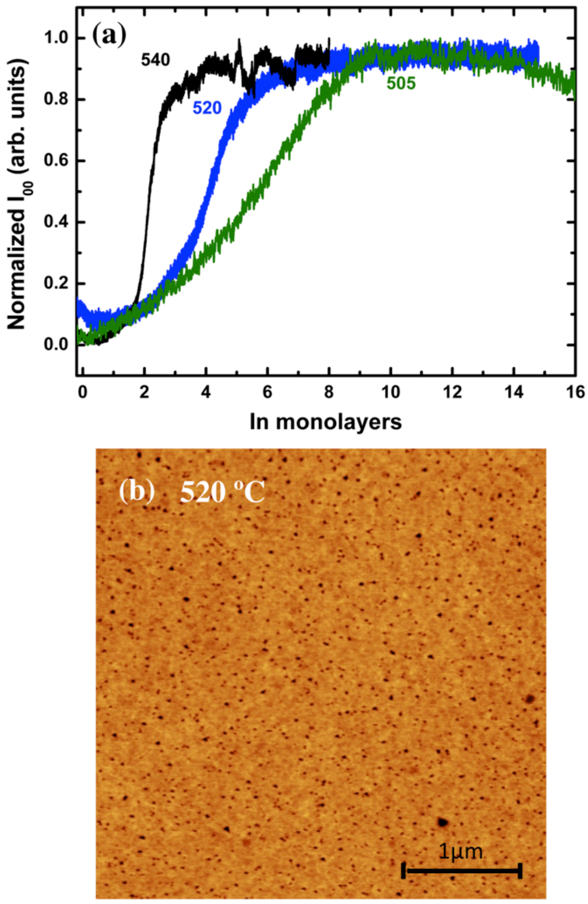
0
1
2
3
4
5
6
7
Ga monolayers
(b) 520 ºC
1µm

Fig. 2.


(a)
540
520
505
Normalized I₀₀ (arb. units)
1.0
0.8
0.6
0.4
0.2
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0
2
4
6
8
10
12
14
16
In monolayers
(b) 520 °C
1µm

Fig. 3.

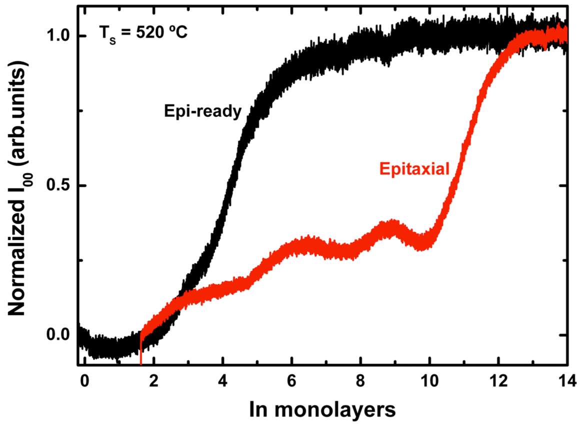
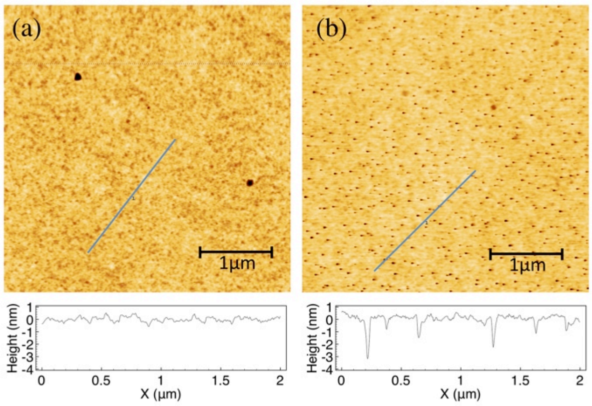

T_s = 520 °C
Epi-ready
Epitaxial
Normalized I_00 (arb.units)
1.0
0.5
0.0
0
2
4
6
8
10
12
14
In monolayers

Fig. 4.


(a)
(b)
1µm
1µm
Height (nm)
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0
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-2
-3
-4
X (µm)
0
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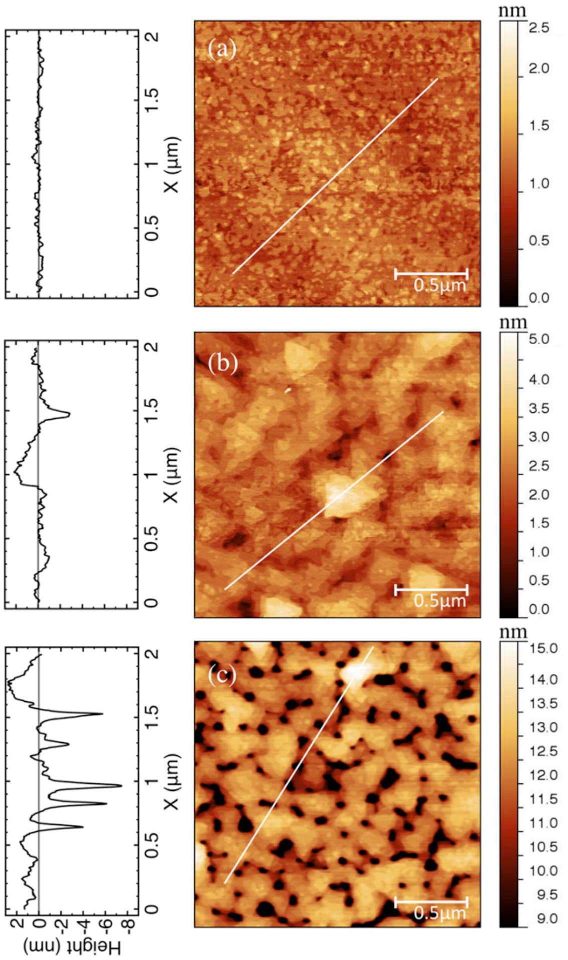
1
1.5
2

Fig. 5


(a)
(b)
(c)
0.5µm
0.5µm
0.5µm
nm
2.5
2.0
1.5
1.0
0.5
0.0
nm
5.0
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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nm
15.0
14.0
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
X (µm)
0
0.5
1
1.5
2
Height (nm)
2
0
-2
-4
-6
-8

Fig. 6.