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# InP patterning using contact mode and non-contact AFM lithography for quantum dot localization

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**Abstract**

AFM contact and non-contact mode have been used to oxidize InP(001) surface at the nanoscale in order to create, after oxide etching, nano-holes used as nucleation sites for self-assembled quantum dots (QDs). Results obtained in contact mode are similar to those obtained with the local anodization of silicon, and principally explained by the effect of space charges that occurs during the initial stages of the oxide growth. Using a negative pulse permits the experimenter to reduce the space charge effects in the oxide and thus to enhance both homogeneity and resolution. Non-contact mode coupled with a modulated voltage brings even more specific results. For more than two a decade variation of probe velocity (0.01–5 μm $s^{-1}$), the AFM oxidation introduces no significant changes in the features. Studies on the influence of oxidation time have identified two regimes. With the first one, a high growth rate was found for oxidation times shorter than 100 ms. Second, for oxidation times longer than 100 ms, we observe an oxide height saturation and a lower lateral growth rate. These results provide a way to control separately both depth and diameter of holes. The achievement of non-contact oxidation confirms the compatibility of this technique in both resolution and homogeneity for QD nucleation sites.
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*Keywords:* Nanopatterning; AFM; Local anodization; III–V semiconductors; Quantum dots; Nucleation site

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## 0. Introduction

The first work of Dagata [1] proved the possibilities of scanning probe microscopy (SPM) to induce nanoscale surface modifications. Since this early achievement, a lot of work has been done to understand and improve the local anodization mechanisms [2–4]. The greatest enhancement in resolution came from the use of modulated voltages [3] and the possibilities of anodization in non-contact mode [4]. They give an easy way to locally modify the surface in a non-destructive manner, opening the way to nanopatterning. Coupling the latter with the Stranski–Krastanov growth mode [5] (well-known to provide high quality quantum dots) then allows for great improvement in QD characteristics such as narrow size distribution and controlled densities. Moreover, it permits an accurate control of QD spatial localization [6].

In this paper, we report on InP surface patterning by atomic force microscopy (AFM) in order to localize InAs QDs, a task of prime interest for 1.55 μm wavelength emitting systems. The principle of the patterning is to grow oxide plots under an AFM tip and then to etch them to create nano-holes suitable for InAs QD nucleation sites. According to our knowledge, we carried out the first application of local anodization on InP surface. To achieve this purpose, two techniques were used. The first one is a standard local anodization, which employs contact mode with constant voltages. The second one uses an original and unusual combination of intermittent contact mode (also named non-contact mode) with a modulated voltage. We present here the results obtained with these two techniques in order to achieve compatible hole size, typically in the 10–20 nm range, for InAs QD nucleation sites.

## 1. Experiment details

Samples investigated were grown on n doped ($4 \times 10^{18}$ cm$^{-3}$) InP epi-ready wafers. To control both height and width of the oxide structures, we needed to decrease the substrate roughness. This was obtained, by growing epitaxially a 300 nm thick n doped ($2 \times 10^{18}$ cm$^{-3}$) buffer layer. Roughness was thus decreased from 0.65 to 0.3 nm rms. Then, we used a two step InP surface cleaning process consisting of an acetone/water ultrasonic bath followed by a 60 s dip in 5% aqueous HF. Samples were then rinsed using deionized water. This procedure is also used to etch the oxide pattern in order to obtain the replica of our oxide patterns.

Our apparatus consists of a commercial Nanoscope III from Digital Instruments operating in contact and intermittent contact mode with an additional bias circuit to perform oxidation and electrical characterizations. Standard $PtIr_5$ coated silicon cantilevers with a resistivity of 0.01 Ω cm were used. The average spring constant and resonance frequency were about 0.2 N/m and 13 kHz, in contact mode, and 2.8 N/m and 75 kHz in intermittent contact mode, respectively. Oxide features were realized in air with a relative humidity remaining between 70% and 80%. Voltage was applied to the substrate for both contact and intermittent contact modes. In intermittent contact, the oxidation was initiated by a decrease of the oscillating amplitude of the cantilever, an AC modulated voltage applied during all the experiments (Fig. 1). Standard set-up conditions are presented in Table 1 for both modes.

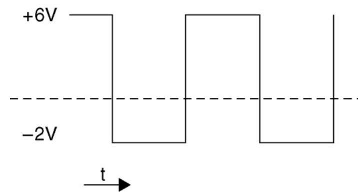


Fig. 1. Scheme of modulated voltage used in intermittent contact mode.

Table 1
Operating conditions used for the AFM anodization

| | Static oxidation (for oxide plots) | Dynamic oxidation (for oxide lines) |
|---|---|---|
| Contact mode | 0–12 V constant voltage<br>1–100 s pulse duration | 0–12 V constant voltage<br>0.001–0.1 μm $s^{-1}$ |
| Intermittent contact mode | $V_{positive} = 6$ V<br>$V_{negative} = -2$ V<br>Frequency = 1 kHz<br>1 ms–1 s pulse duration<br>1.5 nm cantilever oscillating amplitude | $V_{positive}/V_{negative} = 3$<br>$V_{positive} = 2$–12 V<br>Frequency = 1 kHz<br>1.5–150 nm cantilever oscillating amplitude |

## 2. Contact mode

According to our knowledge, local anodization mechanisms, widely studied on silicon, were unknown on InP. To develop this technique and obtain compatible results with QD localization, we have first chosen to develop standard contact mode oxidation. This method uses an electrochemical reaction induced by a positive voltage applied on the substrate. This electrochemical reaction could be identified as a usual anodization reaction [7]: $InP + 8h^{+} + 4OH^{-} \rightarrow InPO_4 + 4H^{+}$. This reaction induces a double-fold increase in material volume (between 85% and 108% of increasing). It generates a surface modification that can be observed on topographic images. This oxide feature is specifically etched to obtain nano-holes as nucleation sites. A complete study was realized to achieve features, such as those presented in Fig. 2. We characterized the local oxidation in terms of kinetic and topographical results. Fig. 3 exhibits a height dependence of the oxide features with oxidation time (voltage duration). We found that in the 1–100 s time range, the height increase followed a logarithmic law. A study of the oxide size dependence with tip velocity (Fig. 4) corroborates these results. We also obtained a logarithmic law with respect to tip velocity in the 0.01–1 μm $s^{-1}$ range. These two results agree well with the local anodization law found for silicon, and they are assumed to be due to space charge effects that occur during the initial stages of the oxide growth [7]. Similar agreement with the silicon anodization law has also been found for the study of size of oxide features versus voltage: The oxide width and height followed a linear law with voltage variation (Fig. 5). However, we found that this linear evolution ranged from 0 to 12 V with no

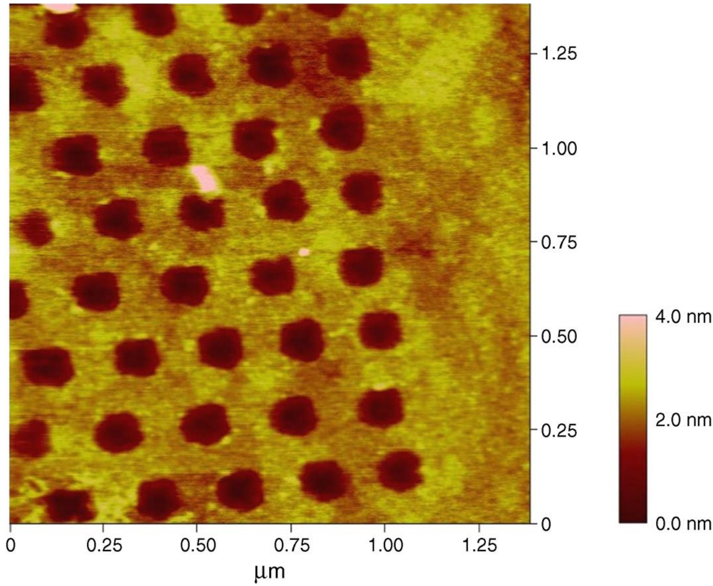


Fig. 2. Nanopattern realized in contact mode, after oxide plot etching. A 6 V voltage was applied during 0.5 s. The size of the holes was 1.8 ± 0.3 nm in depth and 70 ± 11 nm in width.

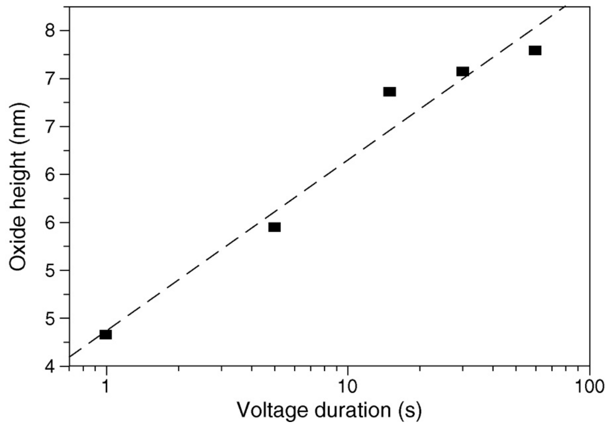


Fig. 3. Oxide height dependence versus oxidation time in contact mode.

observation of voltage threshold in contrast to what has been observed with silicon. This voltage threshold found in silicon is connected to the desorption of atomic hydrogen that passivates the surface [8]. We explain our results by a non-homogeneity of the hydrogen covering which in turn permits oxidation without any voltage threshold.

We also investigated the possibilities of AFM contact oxidation in terms of reproducibility and homogeneity. To make data statistics, we used an array of twenty five

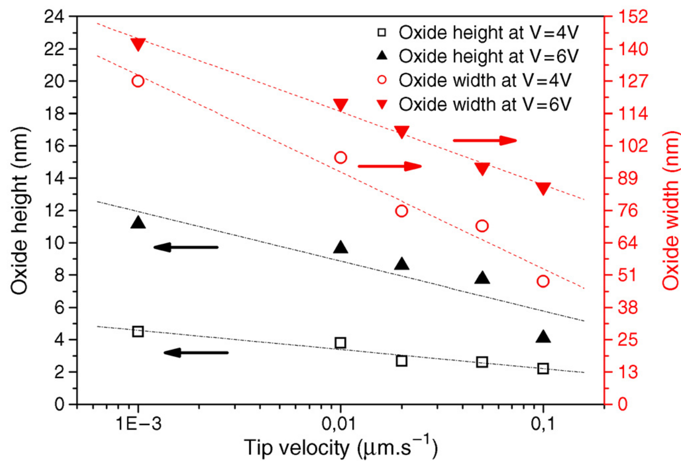


Fig. 4. Oxide dot size dependence versus tip velocity for two different voltages in contact mode.

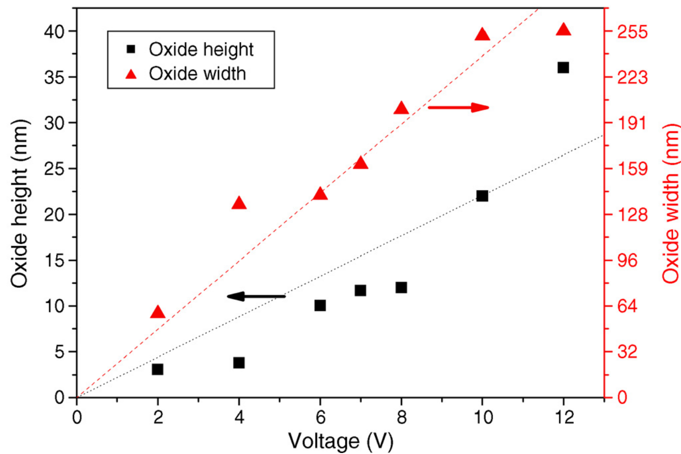


Fig. 5. Oxide dot size dependence versus voltage in contact mode. The probe velocity during the oxidation was maintained at 0.01 $\mu$m s$^{-1}$.

oxide plots separated by a 150 nm distance. The first test was realized in standard mode using a 6 V voltage pulse during 0.2 s. The tip velocity used between two voltage pulses was 0.1 $\mu$m s$^{-1}$. A poor homogeneity is observed and the oxide plots are contiguous. After etching we obtained holes of $3 \pm 3$ nm in depth and $53 \pm 26$ nm in diameter. The poor plot size homogeneity is related to field effect diffusion of the oxyanions present in the oxide. After the voltage pulse the oxide is charged by oxyanions that freely diffuse [7]. Due to the short time between two pulses, we had a field effect on the oxyanion diffusion which induces the oxidation between two oxide plots. To reduce these effects, two approaches

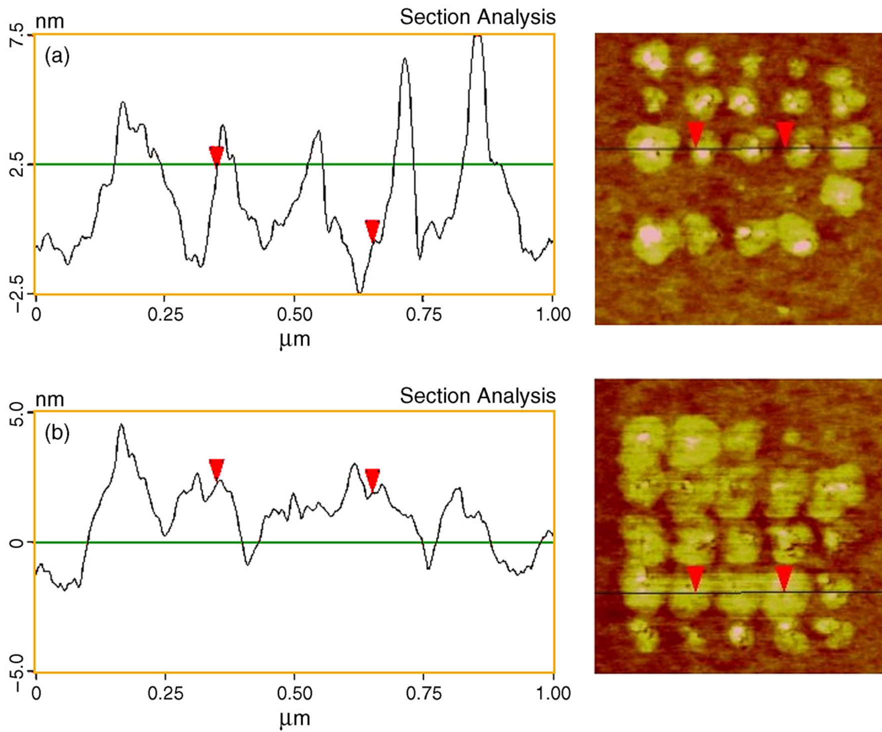


Fig. 6. Oxide patterns realized in the same conditions with (a) or without (b) negative pulse. After etching, we obtained holes with $1.9 \pm 1.1$ and $1.1 \pm 0.8$ nm in depth and $87 \pm 25$ and $74 \pm 23$ nm in width, respectively.

were explored. The first one consists in decreasing the tip velocity between two pulses, to allow enough time for a free diffusion of the oxyanion. For the second one, a negative pulse is applied after each positive one. This second pulse removes the oxyanions and thus stops the diffusion. Both approaches led to an improvement of the oxide plot homogeneity. We obtained an improvement of 75% both in depth ($1.9 \pm 1.1$ nm) and width ($87 \pm 25$ nm) for a velocity of 0.05 $\mu m\ s^{-1}$ and 47% ($1.1 \pm 0.8$ nm) and 58% ($74 \pm 23$ nm) for depth and width, respectively, using a $-6$ V pulse during 0.5 s (Fig. 6). The second approach offers, in addition to a better homogeneity, an improvement of the lateral resolution. That can be explained by the reduction of the lateral oxyanion diffusion.

We showed that relatively good homogeneity can be obtained via this contact mode technique. However, for further improvement of the resolution, we have developed another technique using intermittent contact mode coupled with AC modulated voltage.

## 3. Intermittent contact mode

AC modulated voltage is used to limit the space charge effects during the oxide growth [7]. The intermittent contact mode allows for a reduction of wear of the probe

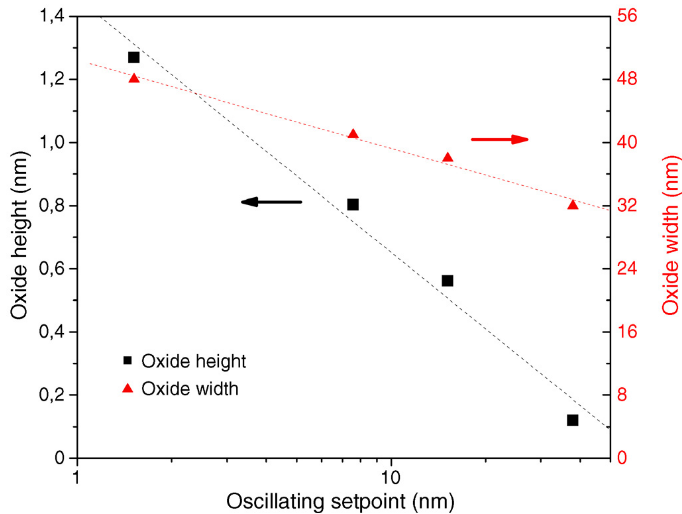


Fig. 7. Oxide dot size dependence versus oscillating setpoint.

during the oxidation and for a better control of the water meniscus [4]. We first investigated the oxide height and width dependence versus voltage applied while keeping constant the ratio between positive and negative amplitudes. The experiment was realized from +2/−0.66 to +11/−3.66 V. With an increase of the electric field, oxide characteristics present a linear response just as in the case of contact mode oxidation. These results are corroborated by the study, under the same conditions, of the oxide plot size dependence versus probe oscillating amplitude. A decrease in the oscillation amplitude led to a linear increase of the oxide plot size (Fig. 7). This can be clearly related to an enhancement of the electric field due to the reduced probe/surface mean distance as the oscillating amplitude is decreased.

The oxide plot size dependence with velocity presents more original results. Indeed, no significant modification of the oxide characteristics can be observed over a range of velocity larger than two decades (0.01–5 $\mu$m s$^{-1}$) (Fig. 8.). These results are understood considering the influence of oxidation time shown in Fig. 9. First, a high growth rate for height and width was found for oxidation times shorter than 100 ms. Then, for oxidation times longer than 100 ms, we observed a height saturation and a lower lateral growth rate. This could be directly related to the use of the modulated voltage. Indeed, the anions can only diffuse during the positive part of the applied voltage [7], whereas the negative part removes them. Consequently, the diffusion depth is limited which leads to the observed saturation effects. Concerning the width, we must consider that the ions are constrained by the electric field, so they cannot freely diffuse on the sides of the feature. This explains the saturation effect observed with the velocity and also the reducing oxide lateral growth rate with the oxidation time. This saturation effect then allowed us to accurately control the oxide plot sizes: we realized a hundred oxide plot array showing very good homogeneity (1.3 ± 0.3 nm in height and 27.6 ± 3.1 nm in width). After etching, we achieved an array

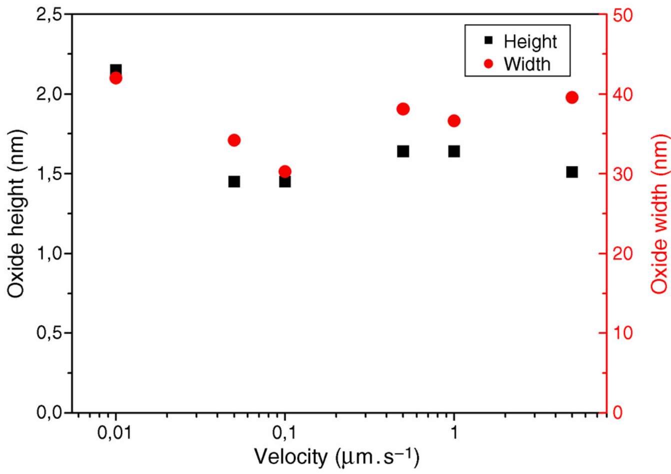


Fig. 8. Oxide dot size dependence versus tip velocity. A standard voltage of +6/−2 V at 1 kHz was used.

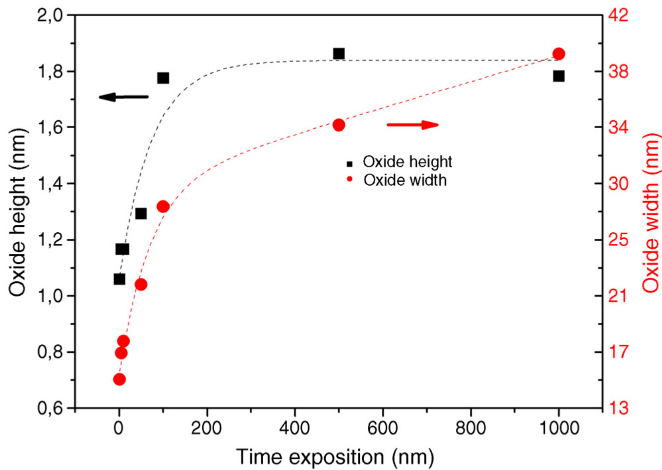


Fig. 9. Oxide dot size dependence versus oxidation time. A standard voltage of +6/−2 V at 1 kHz was used.

of holes, $1.1 \pm 0.2$ nm in depth and $24.3 \pm 3.9$ nm in width (Fig. 10), that could be suitable to localize QDs. InAs QD growth on such patterned InP surfaces is under progress.

## 4. Conclusion

AFM anodization is shown to be a suitable technique to fabricate nucleation sites for QDs. Contact mode anodization provides, even with the improvements presented, too large feature sizes for this purpose. To increase both the resolution and homogeneity, non-contact

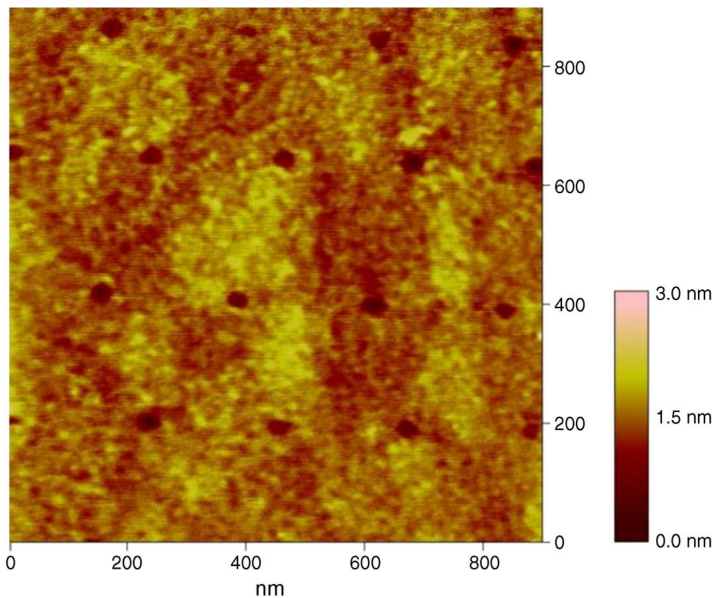


Fig. 10. Nanopattern realized in intermittent contact mode after the etching of the oxide plots. A $+6/-2$ V modulated voltage was applied during 100 ms. The size of the holes was $1.1 \pm 0.2$ nm in depth and $24.3 \pm 3.9$ nm in width.

mode is more appropriate. Moreover, this mode brings, at a nanoscale resolution, the possibility to control separately depth and diameter of the nucleation sites.

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