The influence of humidity on the kinetics of local anodic oxidation

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Abstract. In this paper the influence of relative humidity on fabrication of nanostructures at GaAs (100) surfaces by local anodic oxidation (LAO) is reported. The attention was paid both to the dimensions of oxide nanolines prepared at different relative humidities for tip-sample voltages of 6 - 9 V and tip speeds of 10 - 200 nm/s, and to the profiles corresponding to line trenches (etched in HCl after the nanoxidation). Contrary to the expectations the height and the half-width of oxide nanolines did not increase with relative humidity in the whole interval from 35% to 90%, but for lower relative humidities (< 50%) the lines were comparable in size to those prepared at 90%. However, this was accompanied with instabilities in the oxidation process resulting most probably from enhanced size variations of the water meniscus between the tip and the surface at these low humidities.

1. Introduction
Local anodic oxidation (LAO) carried out by AFM has become a favorite tool for building oxide insulating nanostructures on a variety of conductive and semi-conductive surfaces at laboratory conditions. Such structures can be used as the main building blocks for the fabrication of a variety of nanoelectronic and nanophotonic devices [1] which are intensively studied nowadays. Nevertheless, the properties and efficiency of such devices have been strongly influenced by dimensions of oxide nanostructures which should be as small as possible.

From these reasons the influence of operational parameters on nano-oxidation, such as tip-sample voltage, tip writing speed, and tip load force, has been already studied using contact and non-contact modes of AFM [2]. Contrary to that, less attention has been paid to the role of relative humidity in this process and just few exact and detailed humidity dependences have been published yet (e. g. for n-Si(100) [3] and p-Si(100) [4]).

In this paper the influence of relative humidity on fabrication of nanostructures at GaAs (100) surfaces by LAO is reported. In addition to the size of nanostructures the attention has been also paid to the role of relative humidity and surface roughness on the formation of a water meniscus between the tip and the surface.

2. Experimental details and principles
All the experiments were performed using an atomic force microscope (AutoProbe CP-R, Veeco) operated in the contact mode. In case of nanolithography triangular silicon cantilevers (Micromash)
with a W₂C coated tip and the average force constant 0.35 N/m were applied. The real tip-apex radii found by SEM (FEI) were in the range from 50 nm to 108 nm. On the other hand, rectangular phosphorus-doped silicon cantilevers (VEECO) with the average force constant 0.9 N/m and radius below 12.5 nm were used for spectroscopy measurements.

The GaAs(100) substrates doped by Si (7 x 10¹⁷ atoms/cm³) with a resistivity of 10 Ω·cm were used for the measurements. The surface had not been treated before oxidation and its root-mean-square surface roughness (RMS) was 1.04 nm and average surface roughness (Ra) 1.34 nm.

The principle of the local anodic oxidation process performed by AFM is schematically shown in Figure 1. In this technique oxides locally grow on a chemically reactive substrate by the application of a voltage between a conductive AFM tip and a substrate surface which acts as an anode. Oxyanions (OH⁻ and O²⁻) contribute to the formation of surface oxides and, due to an electric field-enhanced diffusion through the oxide layer, also to the growth of the oxides underneath [5 - 8].

Except voltage and oxidation time the LAO process strongly depends on the amount of adsorbed water and on the water bridge between the tip and the surface (Fig. 1), as discussed in [3, 6, 9, 10]. Both these latter factors are influenced by relative humidity because water on hydrophilic surfaces spontaneously condense from vapour into pores and cracks on the surface and under the tip.

Figure 1: Local anodic oxidation by AFM: Water bridge between the tip and the surface and the values of the Kelvin radius for different relative humidity.

3. Results and discussion
To quantify the influence of relative humidity, testing arrays of nanolines were fabricated. In Figure 2 an example of such an array of oxide lines on GaAs made under a relative humidity of 90% and a temperature of 22 °C is depicted. Going from left to right in this picture one can see the lines prepared at progressively decreasing writing speeds. On the other hand, going from bottom to top, the lines made at progressively higher tip-sample voltages are present. It is obvious that the line prepared at the highest tip-sample voltage and the lowest writing speed (top-right) is the best developed one in height and width. On the other hand, the line fabricated at the lowest tip-sample voltage and highest writing speed (bottom-left) is less developed. Such arrays of testing lines were fabricated at different relative humidities ranging from 35% to 90% to find the relations between the size of nanostructures and relative humidity. After oxidation the samples were etched in 5% solution of HCl to remove the oxide lines selectively and find out the depth of oxidation.
In Figure 3, the height of oxide nanolines on GaAs(100) made at the tip writing speed 10 nm/s and depth of etched nanotrenches are depicted as a function of tip-sample voltage for five different values of humidity. The height of the oxide lines was read and averaged from the AFM images. The error bars represent its standard deviations. The height of oxide lines for humidities 40%, 60%, 75% and 90% shows a linear dependence on tip-sample voltage which is in agreement with the Cabrera-Mott theory [6, 7]. The linear dependence was not observed for the relative humidity 35%. It can be seen that for the relative humidities 40%, 60%, 75% and 90% the oxide heights progressively increase with humidity. This common tendency is disturbed again at the relative humidity 35% where the height values are even twice bigger than those for 90%. This is in contradiction with the expectations that the dimensions of oxide lines progressively grow with relative humidity. One can observe much bigger standard deviations (error bars) of height at this low-humidity curve. Such behaviour was not unique in our experiments and appeared regularly for the relative humidity range from 35% to 45%. The depth of nanotrenches revealed a similar tendency but the humidity dependences are not so obvious. It is caused by an increase of roughness of sample surfaces after its etching in HCl as can be partially seen from the standard deviations of depth values.

In Figure 4 the half-width of oxide nanolines on GaAs(100) as a function of tip-sample voltage for five different relative humidities and for writing speed 10 nm/s is shown. The half-widths were determined as an average width at half of oxide line heights read from the AFM images. These values at the relative humidities 60%, 75% and 90% roughly show up a linear dependence on tip-sample voltage as in our previous experiments [11] and grow with increasing relative humidity. This tendency is broken at relative humidities of 35% and 45% again. The half-width values at 35% are dispersed over a large value range, at 40% they are even bigger than those at 90% and show up a decreasing tendency with higher tip-sample voltages. Such deviations from expected results were observable even at higher speeds (20 nm/s, 50 nm/s, 100 nm/s, 150 nm/s and 200 nm/s) and in all cases they appeared at the lowest relative humidities (35% - 45%), similarly to the oxide-line heights.

Hence, the experiments have not proved the height and the half-width of oxide nanolines increase with relative humidity in the whole interval ranging from 35% to 90%. At the same time big deviations in line dimensions (height, half-width) for relative humidities around 40% appeared along the nanolines themselves. This indicates instabilities of the oxidation process at lower humidities. The process and dimensions of nanostructures became stabilized at relative humidities above 50%. This fact is very well observable in Figure 5 where the AFM images for a relative humidity of 45% and 75%, are presented. To understand why the oxidation process is unstable at lower humidities and stable at values over 50%, further studies based on the AFM force-distance spectroscopy together with computer simulations of the water meniscus and electric field modified by this meniscus have been carried out. The results indicate that instabilities in the oxidation process are most probably
caused by enhanced variations of the size of the water meniscus between the tip and the surface at lower relative humidities. Presentation of these results goes beyond the scope of this paper and will be discussed elsewhere.

Figure 3: The height of oxide lines and depth of etched nanotrenches on GaAs(100) as a function of tip-sample voltage for five different values of relative humidity (writing speed 10 nm/s).

Figure 4: The half-width of oxide lines on GaAs(100) as a function of tip-sample voltage for five different values of relative humidity (writing speed 10 nm/s).
4. Conclusion
It was shown that the height and half-width of oxide nanolines do not increase with relative humidity in the whole interval ranging from 35% to 90%. Unexpectedly, for low relative humidities (<50%) the lines comparable in the size to those prepared at 90% were obtained. However, the big deviations in line height and half-width for these humidities were observed along the individual nanolines. This indicates instabilities in the oxidation process which most probably are caused by enhanced size variations of the water meniscus between the tip and the surface at lower relative humidities. The spectroscopy measurements and simulations of the water meniscus between the tip and the surface support this idea and will be published elsewhere.

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6. References
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