



# The deepness enhancing of an AFM-tip induced surface nanomodification

D.V. Sheglov<sup>a,b,\*</sup>, A.V. Latyshev<sup>a,b</sup>, A.L. Aseev<sup>a</sup>

<sup>a</sup>*Institute of Semiconductor Physics SB RAS, Novosibirsk 630090, Russia*

<sup>b</sup>*Novosibirsk State University, Novosibirsk 630090, Russia*

Received 31 May 2004; received in revised form 6 September 2004; accepted 9 September 2004

Available online 19 November 2004

## Abstract

The novel method of the semiconductor nanostructuring (TINE&MEMO) has been developed on the base of the simultaneous AFM-tip induced local anodic oxidation and mechanical modification of the surface under the applying of advanced electric potentials. The TINE&MEMO-based technology allows obtaining the principle new scale of the depth up to 100 nm for the nanostructure fabrication with a low aspect relation between the width and deepness. The developed nanoscale AFM-lithography has been clearly demonstrated on titanium, gallium arsenide and silicon substrates for creation of electronic nanodevices.

© 2004 Elsevier B.V. All rights reserved.

PACS: 81.16.Nd; 68.37.Ps

Keywords: AFM; Nanostructuring; Local anodic oxidation; Surface nanomodification

The modern nanoscience progress is generally depended on the nanostructure fabrication and structural characterization with an atomic resolution. One of the promising candidates for the practice diagnostic and perspective nanolithography is a scanning probe microscopy (SPM) having a mutual family of instruments, which were performed for the large number of theoretical and experimental studies over the last decade [1]. It was the aim of this paper to cover some

advantages of an atomic force microscopy (AFM) in the areas of the nanostructure lithography based on probe-induced surface modifications for the fabrication of electronic devices.

An atomic force microscope (Solver P-47H, NT-MDT, Russia) has been adapted to carry out lithographical experiments at ambient conditions. The both contact and semi-contact (frequency-modulation) modes were performed using conductive silicon cantilevers with a resonance eigenfrequency of 150–450 kHz.

One of the most common SPM-based nanolithography methods is the AFM-tip induced local anodic

\* Corresponding author. Tel.: +7 3832 344082; fax: +7 3832 331080.

E-mail address: [sheglov@thermo.isp.nsc.ru](mailto:sheglov@thermo.isp.nsc.ru) (D.V. Sheglov).

oxidation of the surface under the applying, negative, respectively, to the surface, of an electric potential. At the humid atmosphere a high electrostatic field ( $\approx 10^8$  V/cm) near the AFM-tip produces the set of oxygen-bearing anions, which are reacted with surface atoms. Unfortunately there is not a universal theoretical model, which can explain the registered kinetic of an oxidation. So we carried out precision experiments on a local anodic oxidation significantly depended on an anodic potential, initiated pulse duration, air humidity and type of the oxidized material (Si, GaAs, Ti).

The coarsen relief of the substrate, several nanometers in the height, may cause the significant experimental errors for measurements of AFM modifications having the same order scale. In this reason special procedures were applied to the substrate achieving surface areas with the smallest roughness [2,3]. For example, large atomically flat silicon substrates with the average roughness less than 0.1 nm were prepared by the optimizing of heating conditions during the thermal annealing in an UHV chamber.

To obtain clarifications of basic mechanisms of the AFM-tip induced anodic oxidation, the kinetics of the oxide line growth was studied in detail for Ti, Si, GaAs surfaces and for the ultrathin titanium film (4 nm) on the silicon (Fig. 1). The oxidation height was evaluated from the topographical AFM-image of oxidized line sets as shown in Fig. 2 for the titanium surface. The oxidized lines were formed with the increasing of the magnitude (from the left to right) and

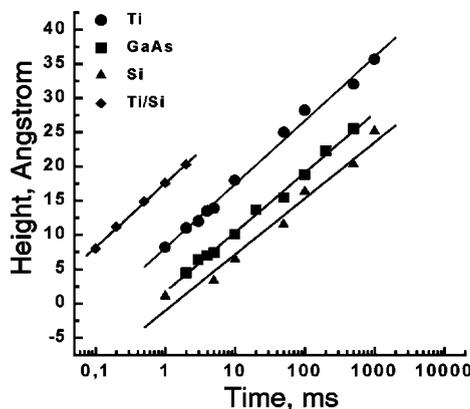


Fig. 1. Temporal dependence of the oxide line height under applying of 10 V potential at AFM-tip for different substrates.

pulse duration (from the bottom to top) of an applied anodic potential at the point. Oxide patterns were easily visualized by an AFM due to the oxide line swelling (volume expansion) leading to the local increasing of the relief height of the oxidized area because the molecular volume of an oxide is higher than a crystal one.

The height-temporal dependence can be approximated in good agreements with the first Mott model of an oxidation as  $h = h_c \ln \left[ \frac{t}{t_c} \right]$ , where  $h$  is a oxidized line height,  $h_c$  a some length characterized by an electron exchange energy,  $t$  an oxidation time and  $t_c$  a threshold oxidation time [4]. The linear relationship between the oxide height and applied voltage is a known fact whereas the variation of the oxide height has been measured as  $h \propto \ln [t]$ [5,6] or  $h \propto t^{1/n}$ [7,8].

Using a logarithmic model, it may be predicted the growth rate to be proportional to  $\frac{dh}{dt} \propto \exp \left[ -\frac{h}{h_c} \right]$ , where  $h_c$  is a characteristic length equaled to  $\approx 1$  nm [9]. From the expression proposed by Cabrera and Mott [10] for the growth rate, the inversely logarithmic dependence was easily deduced  $h \propto -\frac{1}{\ln [t]}$  or  $\frac{dh}{dt} \propto \exp \left[ \frac{h_c}{h} \right]$ , where  $h_c \approx 10$  nm [11].

According to the Fromhold theory [12], the logarithmic law of the oxide thickness growth denotes that the oxidation process is critically regulated by electron exchanges. The threshold oxidation times for Ti, GaAs and Si surfaces were recognized as  $1.4 \times 10^{-4}$ ,  $6.5 \times 10^{-4}$  and  $14.5 \times 10^{-4}$  s, respectively, for the applied voltage of  $-10$  V. The threshold oxide height for that materials was deduced to be the same  $h_c = 0.38 \pm 0.06$  nm. From threshold oxide height, electron percolation energies were estimated easily  $\chi_0 = \frac{h_c^2}{8m\hbar^2}$  to be equal  $65 \pm 20$  meV. Thus the type of the modified substrate does not impact on the basic elementary process of the electron percolation under the Mott's mechanism of an anodic oxidation. The variation of the oxidation kinetics between different substrates was found at threshold times only. But the one order difference in the threshold time for Ti and Si surfaces is depressed by a logarithm dependence at the growth rate. On this basis we speculate that for the valuable increasing of an anodic oxidation rate it is necessary to enlarge  $h_c$ . This conclusion is justified by obtained anodic oxidation results including mutual published results on GaAs [13], Si [14], Ta [15], Al [16,17] and Ti [18,19] films, which are declared that an AFM-nanolithography is

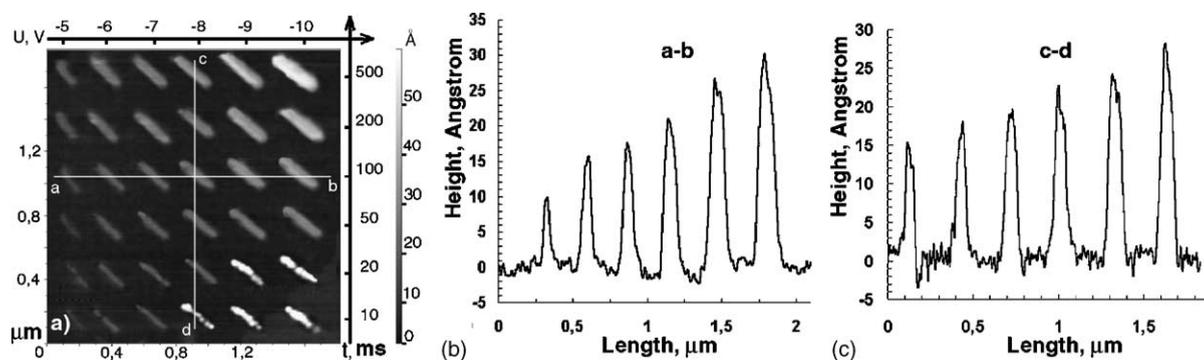


Fig. 2. Topographical AFM-image of titanium film on the silicon(1 1 1) substrate with the set of the anodic oxidized lines (a). The applied potential time and voltage magnitude were increased from bottom to top and from left to right, correspondingly. Relief profiles along the a–b (b) and c–d (c) lines.

drastically limited by a small depth of the surface oxidation ( $< 10$  nm) at standard conditions.

Moreover, an AFM tip-induced modification method based on the direct mechanical action to the surface (direct scratching) does not allow obtaining a resolution larger  $\approx 2$  nm in depth before the critical tip deconvolution occurred even for a relatively soft surface [20].

The oxidation kinetics and oxide line structure allow us to evaluate three basic limiting factors for an AFM-tip induced oxidation process. First one is the existence of the natural oxide layer on the surface, which limits the anions diffusion to the bulk. Unfortunately there are no ways to remove completely the natural oxide on the silicon surface for AFM experiments at ambient conditions. Additionally an atomic clean surface obtained at UHV conditions is free from an adsorbed water making principal impossible the local anodic oxidation by an AFM-lithography [9]. Our experiments for the minimization of an oxide cover did not influence effectively on the deepness of an oxidation. However an effect of a natural oxide on the anodic oxidation may be minimized during the well regulated scratching of the surface by a conductive tip under a voltage bias.

The second factor is mechanical stresses in and around a modified volume during the oxide growth, which restricts a cation diffusion to the reaction zone [9]. To minimize the influence of the non-controlled mechanical stress initiated by the increasing of the volume of an oxide comparing to a crystal one, we

proposed to use an oscillation mode for the modification by the tip. The sharp AFM tip contacted mechanically to the oxidized area produces the partially destruction of the oxide film yielding a stress relaxation inside of the bulk near the tip contact. Moreover the defect generation initiated by the mechanical drubbing occurs preferable channels for a charge exchange during an oxidation process, which can increase the deepness of an oxide film.

And third one is the low potential (10 V) applied between the substrate and tip. Experiments with the increasing of the substrate-tip bias stimulated the unstable oxidation and defect generation making the tip-induced modification is non-reproducible. However our studies show that the tip-sample voltage can be enlarge reasonably up to 50 V by the optimizing of the water vapor or adsorbed water by means of the control the humidity conditions [21,22].

Fig. 3a demonstrates the scan profile of the GaAs surface with two oxide lines, which were obtained by the oxidation at the same 10 V potential but with different mechanic presses towards to the surface. The smallest line, 3.1 nm in the height, was obtained at the typical mode of a local anodic oxidation. Whereas the highest oxide line, 10 nm in the height, was obtained at the modification regime under the pressing of the extra force enough to scratch the surface up to 1–2 nm depth even without the applying voltage on the tip. Unfortunately there is a low aspect ratio of obtained lines (height/width  $\approx 0.05$ ), whereas about 30 nm depth of the modification. Thus the simultaneous local

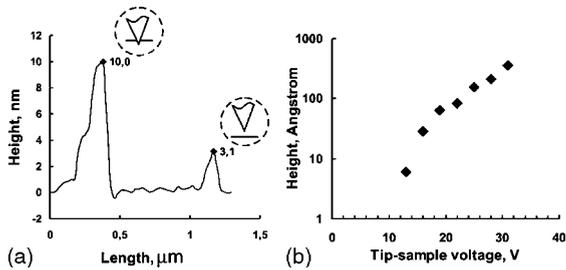


Fig. 3. Cross-sectional relief profile of topographical AFM-image of GaAs surface with two oxidized lines which were grown at the same 10 V potential but with various mechanic stress towards to the surface (a). The left oxidized line, 10 nm in height, was got at a regime of simultaneous surface scratching and anodic oxidation. The right one, 3.1 nm in height, was obtained at standard mode of local anodic oxidation without any mechanic stress. Oxide line height on GaAs surface as a function of applied potential to AFM tip (b).

oxidation and scratching allow to increase the deepness of the modified film comparison to the standard AFM-lithography.

The oxide height dependence on a tip-sample voltage (from 7 to 40 V) is shown in Fig. 3b for an oxidation on the GaAs surface. For realizing of the higher electric voltage, the matched voltage source ( $\pm 50$  V) was developed and integrated into the microscope. One can see that the oxide point height is more than 30 nm (aspect ratio  $\approx 0.3$ ).

The detailed analysis of physical aspects of the AFM-tip induced lithography presented behalf allows us to turn finally to establish the novel method of the simultaneous Tip Induced NanoElectro-MEchanical

Modification (TINE&MEMO). Otherwise it was realized the method of the simultaneous applying to the AFM-tip the both mechanical pressure and electrical bias in an oscillation mode (semi-contacted one), which allows to destroy an natural oxide layer on the surface and annihilate mechanical stresses in the volume.

The TINE&MEMO-based nanolithography was successfully realized for the fabrication of nanoscaled devices [23]. For example, an electron interferometer was fabricated by the figurative cutting of the conductive layer on the heteroepitaxial AlGaAs/GaAs system (Fig. 4). One can see the topographical AFM-image of lithographically defined the electron interferometer with an inner radius less than 100 nm. The analysis of the relief profile along the A–B line shows the oxide line height as near 10 nm (Fig. 4b). The Aaronov–Bohm oscillation period was measured from precision conductivity experiments as corresponded to the effective radius 90 nm. So small interferometer size allows increasing the operational temperature of the device in one order [24].

In conclusion, basic physical mechanisms of the tip-induced local anodic oxidation of Ti, Si and GaAs films at ambient conditions are investigated. The height of oxide patterns is studied as a function of the applied tip-sample voltage and the pulse duration. Energetic parameters for an electron metal-oxide percolation were obtained. The novel TINE&MEMO technology of a lithography based on the simultaneous local anodic oxidation, mechanical scratching and high electric field strength was developed.

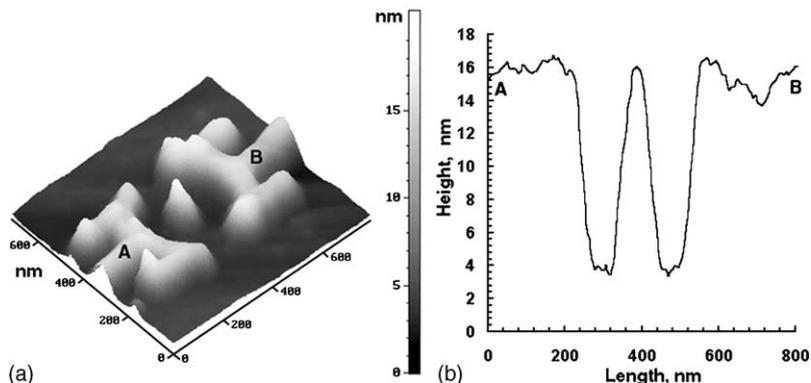


Fig. 4. Topographical AFM-image of AlGaAs surface pattern of an electron interferometer, which was lithographically defined by TINE&MEMO-based technology [24] (a). Line scan through the interferometer (b).

## Acknowledgement

We wish to acknowledge the valuable assistance in experiments of Z.D. Kwon, V.L. Alperovich, S.S. Kosolobov and A.M. Medvedev. AVL thanks “Russian Scientific Foundation”. This work was partly supported by RFBR (16541, 16693), Ministry of Education and Science of Russia (01.01.030, I765/785, A03-2.9-824).

## References

- [1] J.A. Dagata, et al., *Appl. Phys. Lett.* 56 (1990) 2001.
- [2] A.V. Latyshev, A.L. Aseev, *UFN* 10 (1998) 168.
- [3] S.S. Kosolobov, et al., *Phys. Low-Dim. Struct.* 5/6 (2002) 231.
- [4] N.F. Mott, *Trans. Faraday Soc.* 43 (1947) 429.
- [5] H. Sugimura, N. Kitamura, H. Masuhara, *Jpn. J. Appl. Phys.* 1 (33) (1994) 143.
- [6] J. Servat, et al., *J. Vac. Sci. Technol. A* 14 (1996) 1.
- [7] T. Teuschler, et al., *Appl. Phys. Lett.* 66 (1995) 2499.
- [8] E. Dubois, J.-L. Bubbendorff, *J. Appl. Phys.* 87 (2000) 8148.
- [9] P. Avouris, T. Hertel, R. Martel, *Appl. Phys. Lett.* 71 (1997) 285.
- [10] N. Cabrera, N.F. Mott, *Rep. Prog. Phys.* 12 (1949) 163.
- [11] D. Stievenard, P.A. Fontaine, E. Dubois, *Appl. Phys. Lett.* 70 (1997) 3272.
- [12] A.T. Fromhold, *Theory of Metal Oxidation. VI. Fundamentals*, North-Holland, Amsterdam, 1976.
- [13] L.A. Nagahara, T. Thundat, S.M. Lindsay, *Appl. Phys. Lett.* 57 (3) (1990) 270.
- [14] R.K. Workman, C.A. Peterson, D. Sarid, *Surf. Sci.* 423 (1999) 227.
- [15] T. Thundat, et al., *J. Vac. Technol. A* 8 (4) (1990) 3537.
- [16] E.S. Snow, D. Park, P.M. Campbell, *Appl. Phys. Lett.* 69 (1996) 269.
- [17] A. Notargiacomo, et al., *Nanotechnology* 10 (1999) 458.
- [18] H. Sugimura, T. Uchida, N. Kitamura, H. Masuhara, *J. Phys. Chem.* 98 (1994) 4352.
- [19] R. Held, et al., *Physica E* 2 (1998) 748.
- [20] E. Dubois, J.-L. Bubbendorff, *Solid State Electron.* 43 (1999) 1085.
- [21] D.V. Sheglov, *Phys. Low-Dim. Struct.* 5/6 (2002) 239.
- [22] D.V. Sheglov, Yu.V. Nastaushchev, A.V. Latyshev, A.L. Aseev, *Int. J. Nanosci.* 3 (2004) 75.
- [23] D.V. Sheglov, A.V. Latyshev, A.L. Aseev, *AIP Proceedings of the 12th International Conference on Scanning Tunneling Microscopy/Spectroscopy and Related Techniques (CP696)*, 2003.
- [24] V.A. Tkachenko, et al., *JETP Lett.* 93 (3) (2004) 168.