The physical-chemical model of the tip-induced oxidation process on thin metal films, factors influencing and improvement of the lateral resolution.

Lemeshko S.V. Saunin S.A. Roschin V.M. Yalovenko A. Y.
NT-MDT, State research institute of physical problem, Block-B, 124460 Moscow,
Zelenograd, RUSSIA, 095-535-03-05, lemeshko@ntmdt.ru

In a last decade the surface local modification methods by scanning probe microscope actively have developed. There are several ways of the surface properties modification in a nanometer scale by AFM or STM means like, by mechanical scratching or by voltage impulses applying on a tip.

The wide practical applications of probe lithography have been found based on anodization of a surface accelerated by the cantilever tip. The method of tip-induced oxidation of a metal and semiconductor surfaces starts to be used even for nanoelectronic devices creation [1,5].

The method essence is in electrochemical reaction stimulation under the conductive tip with applying of a negative voltage on the tip respectively to a surface. On ambient conditions in case of intimate contact between a tip and a surface in points where voltage have been applied under the tip the oxide hillocks will grow. At a moment there are few approaches in explanation of an oxide grow mechanism at AFM tip stimulation, however two based on electric field oxidation and based on electrochemical anodization are dominating.

In the present work the factors influencing on a tip-induced oxidation process have been investigated and the physical-chemical model of thin metallic films have been suggested. A local tip-induced oxidation and measurements carried out on scanning probe microscope Solver P47 in semi-contact mode. The 1-10 nm thickness thin films of Ti and W deposited on silicon substrate by a method of cathode arc deposition have used for experiments. The noncontact mode silicon cantilevers with W, Pt, W_2C and TiN conductive coatings have used for performing tip-induced oxidation [6].

At a constant voltage between a tip and a surface an electrochemical cell could be imagined as equivalent electric scheme in form of sequential resistances. Than the tip resistance - R_{tip}, adsorbed water resistance – R_{H2O} and oxidizing material R_m remains fixed during oxidizing. At oxide formation only an oxide resistance - R_{ox} is changing.

In analytical form the voltage distribution could be presented as

$$U = U_{circuit} + U_{ox} \qquad (1)$$

It is known [7] that during anodic oxides growing the constant electric field is established. The value of electric field intensity depends on oxide structure and electrolyte. There is the next simple dependence between U_{OX} and electric field intensity.

$$U_{ox} = E \cdot h_{ox} \qquad (2)$$

By using integral form of Faraday low it is possible to evaluate the h_{OX} dependence from anodization duration and electric current density:

$$h_{ox}(t) = \frac{\eta Q A_{ox}}{S \rho_{ox} z F} = \frac{\eta \chi}{S} \int_0^t J(t) dt \qquad (3)$$

Also, it is known that at potentiostatic bias connection during anodic oxide grow observed the exponential decreasing of electric current density. Usually such dependence is explaining as electric field intensity decreasing. However, if we apply to Güntherschulze-Betz equation which is described the dependence between electric field intensity and current density the negligible low dependence of current density in growing oxide has been conferment by numerous experimental results [7].

$$j = a \cdot \exp(bE) \quad (4)$$

If we neglect of electric field changing in growing oxide along with changing of electric current density and do not consider the revising of the metallic film resistance during its oxidation the anodization parameters can be described as:

$$U(t) = U_c(t) + U_{ox}(t) = J(t)R_c + \frac{E\chi}{S}\int_0^t J(t)dt \quad (5)$$

Rc- the total resistance of an electrochemical cell excluding R_{ox}.

The solution of equation (5) at condition that in a moment t=0 the voltage drops only on resistance of electrochemical circuit.

$$J(t) = \frac{U}{R_c}\exp\left(-\frac{E\chi}{R_c S}t\right) \quad (6)$$

After the substitution of (6) in (3) there is the next equation for oxide height from anodization duration

$$h_{ox}(t) = \frac{U}{E}\left(1 - \exp\left(-\frac{E\chi}{R_c S}t\right)\right) \quad (7)$$

An electrochemical approach of oxide growing kinetic description gives good correspondence between theoretical estimation and experimental results on case of bulk substrates. Obviously, that in case of thin metal films the assumption about constant circuit resistance evenly only for rather short impulse when it is possible to neglect of changing metal film resistance. In the general way this task could be solved by numerical methods.

It have been shown that the tip-induced anodic oxidation start to occur at 20% of relative humidity.

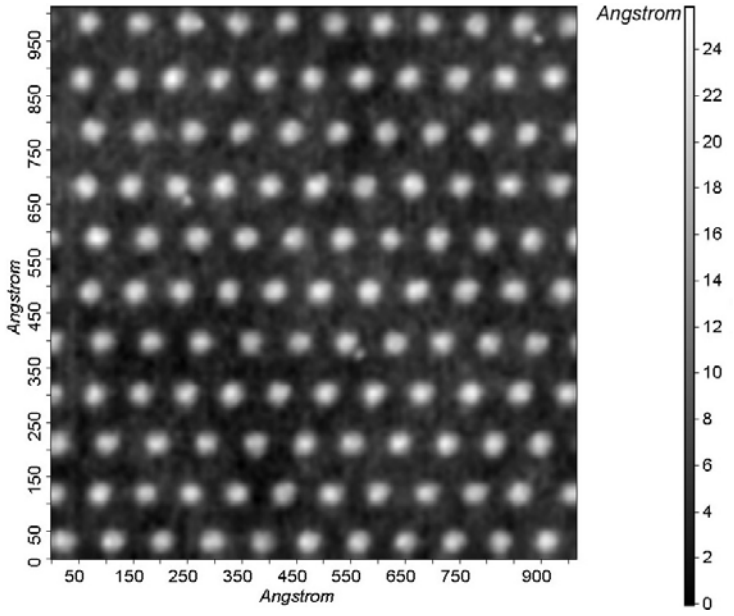

Fig.1. AFM image of 10nm titanium film after tip-induced oxidation at -8V tip bias during 1ms in each point.

In correspondence with suggested physical-chemical model (7) the decreasing of metal film resistance leads to more narrow electric field distribution under the tip and thus leads to oxide line decreasing. On the figure 1 it is shown an AFM image of the 10nm titanium film surface after tip-induced oxidation by using cantilevers with W coating. The mean oxide hillocks diameter is about 4 nm. The experiments with choosing different conductive coatings

have shown that the best results in process resolution achieved on tips with amorphous tungsten coating.

The described technology of high resolution surface patterning is able to be in use for single electron transistors and other quantum device creation which could show performance already on ambient conditions.

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