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Electric field effect on low temperature nanoscale oxidation

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ABSTRACT

The influence of electric fields on the low temperature oxidation of individual nanoscale tungsten wires was investigated. In the experiments at room temperature, the nanowires were biased as anode opposite to a macroscopic cathode and H_2O-vapor with a pressure of 10^{-7}–10^{1} mbar was provided as oxygen source. Under the influence of an electric field, a dramatic change of the oxidation behavior is observed with the formation of several 10 nm thick oxide layers for electric fields exceeding a threshold. The chemical composition of the layers formed is determined with laser-assisted atom probe tomography to be slightly understoichiometric WO_3. After an initial period of fast growth, the oxidation rate later rapidly decreases to immeasurable low values. Evaluation of the electric field distribution in the vicinity of the sample by the finite element method reveals that oxide formation only proceeds if a critical field in the range of 0.7–5.0 V/nm, depending on the H_2O-pressure, is present. This critical field is attributed to a field-activated reaction of H_2O at the oxide–vapor interface. Besides for tungsten, field-induced oxidation is also observed for aluminum and p-doped silicon and thus apparently is a widely material independent phenomenon.

1. Introduction

Surface oxidation is a process that affects almost all metals and semiconductors when exposed to atmosphere. Although oxide formation is thermodynamically strongly favored for most materials, at low temperature the kinetics of the reaction usually decrease to immeasurable low rates after an oxide layer of some nanometer thickness has formed [1]. This is generally attributed to the very low transport rates of the reacting species through the oxide layer. Contrary, the very high initial reaction rate is attributed to electric field-driven transport of anions and cations on the nanometer scale as first proposed by Cabrera and Mott [2,3].

In numerous studies the effect of an external electric field on the oxidation kinetics was investigated. As ionic and electronic currents are coupled due to the need of overall charge neutrality [4] a significant impact on the reaction kinetics is merely achieved when charge is supplied to both oxide surfaces. Accordingly, in previous studies electric fields were applied placing electrodes directly onto the oxide [5–7] or in a distance of some nanometer to the oxide [8–17], or by bombardment of the oxide with electrons [18–22]. Thus, the reactions occurring at the oxide surface are expected to be significantly affected by the experimental conditions. In a different approach, the influence of an electric field on surface oxidation was investigated in a field ion microscope [23–26], but the studies were restricted to the very initial stage of surface oxidation.

In this study, we use free-standing nanoscale wires to elucidate the influence of an electric field on low temperature oxidation. Combining transmission electron microscopy (TEM) and *in situ* current measurements, we quantify the kinetics of the oxidation reaction yielding oxide layers up to some 10 nm thickness. Tungsten, aluminum, and p-doped silicon are chosen as model systems to show that field-induced oxidation is a widely material independent phenomenon. Since ionic species are involved, the driving force and thus the kinetics of the oxidation reaction change significantly under the influence of an electric field as we reported previously [27]. In this study, we focus on the pressure-dependence of the oxidation reaction and deduce the mechanism of field-induced oxidation.

A detailed knowledge of the oxidation behavior of nanoscaled metals and semiconductors is of interest, as any application in atmosphere is reliant on the stability against oxidation. In particular, this is important for the application of nanowires in gas sensors [28,29] and free-standing transistors [30], as in both cases the structures are electrically biased. Thus, the determination of the region of kinetic stability against oxidation in dependence of the electric field strength and the chemical activity of the oxidizing species is a precondition for long-term applications.

For the experiments, nanoscale tips were used instead of ideal nanowires with constant diameter. The advantage in using tips is that their conical shape yields a distribution of the electric field

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strength along the tip with the field decreasing with increasing distance from the tips apex. Thus, the field dependence of the oxidation reaction is easily probed just by applying a constant voltage to the tip.

2. Experimental

Nanoscale tungsten tips were prepared by electrochemical etching of 70 μm tungsten wire (99.9+%) in 2 molar NaOH solution. Platinum was used as counter electrode, and etching was carried out at a decreasing voltage of 7–3 V ac (sinusoid, 50 Hz). The process was observed under an optical microscope and stopped after a sudden decrease of the sample length. That way, a radius of curvature of the nanoscale tip in the range of 10 nm is achieved. Henceforth, the samples where continuously grounded to avoid any unintended electric fields at the sample surface caused by floating potentials.

After etching, the samples were cleaned with methanol and inserted in a field ion microscope [31]. The voltage between the sample and a grounded counter electrode was raised to 5 kV, yielding an electric field sufficient to stripe of sample atoms by field evaporation. This way, protrusions on the sample surface are removed and for all samples the final radius of curvature at the apex is in the range of 10–15 nm. Afterwards, the samples are transferred back to the ambient air where immediately the native oxide layer forms again. Thus, all following experiments are performed with samples which exhibit their native oxide layer. Finally, the samples were characterized using TEM. Only samples with almost cylindrical symmetry (less than 15% deviation between maximal an minimal diameter) were used to study their oxidation behavior.

The oxidation experiments were performed in a vacuum chamber as schematically shown in Fig. 1. The sample is situated opposite to a counter electrode (copper, 60 mm diameter) at an axial distance of 50 mm. A positive voltage V can be applied to the sample with respect to ground. The counter electrode is connected to ground potential via an amperemeter so that the current to ground can be measured. The reactant gas H_2O (vapor over deionized water) is admitted to the chamber through a leak valve.

All experiments were performed at a temperature of 296 K. After adjustment of a certain H_2O-pressure p in the chamber, a voltage V_1 is applied to the sample for the time t_1. By measuring the current an *in situ* monitoring of the oxidation reaction is possible. Subsequently, the sample is transferred back to the ambient air and characterized with TEM. To study the further development, the same sample is inserted into the vacuum chamber again, and at the same pressure p the voltage V_1 is applied for the time t_2. Afterwards, the sample is characterized with TEM once more. Repeating these steps, the total time for the oxidation reaction amounts to $t = \sum t_j$, and due to the characterization with TEM, the sample morphology is known at all times $t_{m,n} = \sum_{j=1}^{n} t_j$.

Furthermore, the dependence of the oxidation reaction on the applied voltage was investigated. For this purpose, the sample is reinserted into the vacuum chamber after the first oxidation step, and at the same pressure p, a voltage V_2 is applied for the time t_1 ($V_2 > V_1$). Afterwards, the sample is again characterized with TEM. Repeating these steps, each voltage V_j is applied to the sample for the time t_1.

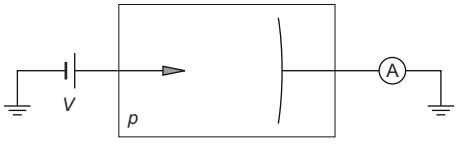

Fig. 1. Schematic drawing of the setup used for the oxidation experiments (base pressure below 10^{-7} mbar).

The chemical composition of the oxide layers formed was determined using laser-assisted atom probe tomography. The analysis was conducted at a sample temperature of 40 K. A laser with 355 nm wavelength, a pulse frequency of 1 kHz, a pulse length of less than 500 ps and a energy density of 20 Jm^{-2} per pulse was used to trigger field evaporation of individual atoms. Further details of the used apparatus may be found in Ref. [32]. As the samples already had a tip-like morphology, the oxidized wires could be analyzed directly without any further preparation.

The electric field in the vicinity of the nanoscale tungsten wires was calculated using the finite element method. The boundary conditions for the calculation are given by the morphology of the samples as determined by TEM and by the experimental setup. In detail, both the metallic part of the sample and the counter electrode define Dirichlet boundary conditions (given electrostatic potential $\Phi = V$ and $\Phi = 0$, respectively). At the remaining free surface of the simulation volume, Neumann boundary conditions $\left(\frac{\partial \Phi}{\partial n} = 0\right)$ are defined. Both, the native oxide and the oxide formed under the influence of the electric field are represented by an isotropic permittivity ε_r. For the gas volume between the electrodes the vacuum permittivity ε_0 is used. Under the premise that no free charges exist in the oxide, the electrostatic potential was determined solving Poisson's equation $\nabla \cdot (\varepsilon_0 \varepsilon_r \nabla \Phi) = 0$ using quadratic basis functions and a size of the finite elements of maximal 0.5 nm in the vicinity of the oxide. The absolute value of the electric field is then given by $E = |\nabla \Phi|$. Because of the symmetry of the samples and the experimental setup, all calculations are performed in cylindrical symmetry.

3. Results

3.1. Introduction to field-induced oxidation

As a survey on the investigated field-induced oxidation, Fig. 2 shows a series of TEM-images of two samples after isochronal stepwise increase of the applied voltage. In the initial state (0 V), the thickness of the natural oxide layer amounts to only two monolayers oxygen [33]. Thus, it cannot be resolved. At sufficiently high voltages, field-induced oxide formation begins, and with increasing voltage the oxidation reaction proceeds. The morphology of the formed oxide reveals a distinct pressure-dependence. For a H_2O-pressure of 10 mbar (Fig. 2b) the oxide has a layer-like morphology, while for a pressure of 10^{-3} mbar (Fig. 2a) it exhibits a cone-like shape. In both cases, a critical radius r_v (defined in

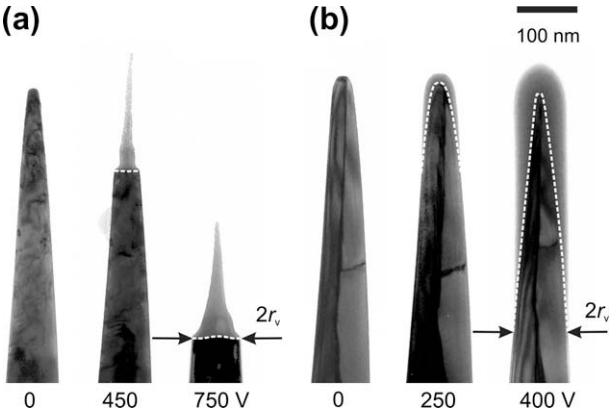

Fig. 2. Series of TEM-images of a nanoscale tungsten tip after the denoted voltages where applied for 10 s at a pressure of (a) 10^{-3} mbar H_2O and (b) 10 mbar H_2O. The interface between metal and oxide is emphasized with a dashed white line. The radius of the tip above which no field-induced oxide formation is observed is indicated as r_v.