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Anodization of titanium in radio frequency oxygen discharge — Microstructure, kinetics & transport mechanism

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ABSTRACT

Plasma anodization in oxygen discharges is a prominent technique in semiconductor processing, allowing nearly defect-free oxidation at low temperatures. Here we apply inductively coupled radio frequency oxygen plasma anodization to titanium and study the effect of temperature and dc bias potential on the oxide film morphology. To achieve a detailed understanding of the growth process, the oxide crystal phase is characterized by Raman spectroscopy and the orientation between the oxide film and the substrate is determined by TEM. The constant voltage oxidation kinetics is modelled and growth experiments with inert markers allow to identify the ionic species controlling the growth rate. Plasma anodization experiments in combination with SIMS depth profiling of the interface region add to these experiments and prove that oxygen is the mobile species in the titania layer. The applied kinetic model allowed the determination of the activation energy for ionic transport with values of 1.31 eV at 200 °C and 1.58 eV at 400 °C and 550 °C. As oxygen ion transport is likely responsible for film growth, the observed surface morphologies were most likely formed by oxygen ion sputtering or result from initial nucleation processes.

1. Introduction

Titanium is a highly versatile metal and used in numerous advanced materials technologies. Due to its high oxygen affinity the titanium surface is usually covered with a protecting TiO_2 film, which may additionally be modified in order to achieve certain functionality. Therefore, quite a number of different techniques for the formation of TiO_2 surface films were developed. Besides deposition techniques like sol–gel coating [1], chemical vapor deposition [2] or plasma spraying [3] direct surface oxidation techniques like thermal [4], electrochemical [5] or plasma oxidation [6] are applied. The latter usually show a better TiO_2 film adhesion, and we will focus on electrochemical assisted plasma oxidation in this paper.

The term “plasma oxidation” usually describes the interaction between an electrically free floating substrate (no externally applied potential) and an oxygen discharge which results in oxide growth close to thermal oxidation [7]. Plasma anodization (or plasma anodic oxidation) is achieved by applying an additional anodic (positive) potential to the substrate, accelerating anions and electrons from the plasma to the sample surface. This process is usually performed in a high frequency discharge and can be considered as a combination of thermal and electrochemical oxidation, as the oxidation is driven by both diffusion (as for thermal oxidation) and migration (as for electrochemical oxidation) of ionic and electronic species. Faster oxide growth is achieved in a temperature range where diffusion-driven growth is almost inhibited because the Nernst–Planck coupling is revoked [8]. As plasmas are mixed ionic and electronic conductors they can serve as electrode and/or electrolyte, providing perfect and homogeneous electric contact. We like to add that plasma anodization is a clean process for the fabrication of nano- or microstructured surfaces as no aqueous medium, catalysts or structure determining ligands are used. Main contaminants only arise from sputter processes which can be prevented by magnetic confinement [9].

A characteristic feature of plasma anodic oxidation is the possibility of field-driven and/or sputter-driven surface structuring, and this is considered as one interesting advantage of this technique. In recent years, two different approaches have been reported for the fabrication of nano- or microstructured surfaces in gas discharges: Vennekamp et al. demonstrated that films growing by outward diffusion of cations will show morphologically unstable growth — leading to regular surface structures — if the film has a higher conductivity than the plasma (sheath) [8,10]. Zheng et al. [11] and Ostrikov et al. [12] obtained e.g. oxide nanowires from Ga, In, Fe and Cd substrates due to the creation of surface ‘hot spots’ where nanowire nucleation is favored.

Following the approach of Vennekamp et al. the more mobile ionic species in TiO_2 will control the growth mode — if titanium ions are more mobile, morphologically unstable (outward) growth can be

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expected; once oxygen ions are more mobile, stable (inward) growth will occur. The defect chemistry and transport properties of TiO_2 have been extensively studied at high temperature [13]. TiO_2 is a nonstoichiometric compound (i.e. it is better described as TiO_{2-x}) in which the ionic majority defect strongly depends on the oxygen activity. At low oxygen activities TiO_2 is oxygen deficient with oxygen vacancies as the major and titanium interstitials as the minor defects [14]. However, at very low oxygen activities it has been observed that titanium interstitials cause significant cation mobility [15]. Since the equilibrium defect disorder and chemical diffusivities at low temperature are unknown, a prediction of the situation for low temperature plasma anodization is not possible a priori, thus, experiments are required. Independent of the field effect, the reaction rate may also be increased compared to thermal oxidation due to plasma assisted activation of surface processes [7].

Although the plasma-surface interactions during plasma anodization are complex due to the presence of numerous neutral, charged, molecular and excited species, there have been various attempts to model the oxidation kinetics in plasma, mainly for silicon. Ligenza reported a linear rate law for thin oxide films, followed by a parabolic rate law for silicon oxidation by using a microwave (μw) discharge [16]. This observation implies that a diffusion-limited process might be responsible for oxide growth. Later, Kraitchman modified this rate law by a negative ("destructive") term due to sputtering of the oxide film [17]. In further studies the formation of a space charge has been suggested to derive an appropriate model [18].

Fromhold et al. developed a theoretical model for plasma oxidation (free floating sample) of lead considering diffusion of ionic species under the influence of space charge in the oxide. The movement of the ionic species was described by hopping equations using the high field limit [19]. Taylor et al. formulated a model for anodization of silicon in radio frequency (RF) and μw oxygen discharges, considering field-driven migration of ions through the oxide layer as the rate determining step and dispensed the high field limit which was not valid for their anodization conditions [20]. A more detailed formulation of this model is given below. Additionally, a solution for a low field approximation was also reported [21]. Other kinetic models were developed based on assumptions about the oxidizing agent being atomic oxygen [22] or neutral molecular oxygen [23] from the discharge.

To our knowledge no studies on the oxidation kinetics and ion transport mechanism for the plasma anodization of titanium exist, and thus we report first data in the present paper. Titanium discs were oxidized and characterized by inductively coupled RF plasma anodization at different temperatures and bias voltages. As it is unclear whether oxygen diffusion is the dominating growth mechanism for plasma grown TiO_2, we marked the oxide/substrate interface with platinum, and by anodization in $^{18}O_2$ plasma (as reported for Si [24]) the oxide growth direction and possible ion transport mechanisms were determined. The kinetics of oxide growth at different temperatures was determined by thickness measurements via SIMS sputter depth profiling. To evaluate these data, the model of Taylor [20], complemented by a sputter term, was used.

2. Plasma anodization theory under constant voltage and space-charge limited conditions

Taylor et al. [20] postulated that the transport of ionic species through the oxide is described by thermally activated hopping over potential barriers of height W, which are separated by a distance a. The corresponding ion flux density J_i is composed of a drift and a diffusion term:

$$J_i = J_{i,\mathrm{drift}} + J_{i,\mathrm{diff}}. \tag{1}$$

Due to a high electric field, the potential barriers are lowered by the amount $qaE(x)/2$ in forward and enhanced in backward direction. q denotes the charge of the moving species and $E(x)$ the electric field strength at a distance x from the surface. If ω_0 is the vibration frequency of the crystal, k the Boltzmann constant, T the sample temperature, $n_i(x)$ the position-dependent ion concentration and E_a the activation energy for ionic transport, the ion flux density $J_{i,\mathrm{drift}}$ can be described in Eq. (2):

$$J_{i,\mathrm{drift}} = 2n_i(x)a\omega_0 \exp\left(-\frac{E_a}{kT}\right)\sinh\left(\frac{E(x)qa}{2kT}\right) \tag{2}$$

As diffusion is neglected in this model, the ion current density j_i can be formulated:

$$j_i = q\cdot J_{i,\mathrm{drift}} = 2qn_i(x)a\omega_0 \exp\left(-\frac{E_a}{kT}\right)\cdot\sinh\left(\frac{E(x)qa}{2kT}\right) \tag{3}$$

To calculate the space charge modified electric field, Poisson's equation is used:

$$\frac{dE(x)}{dx} = -\frac{qn_i(x)}{\varepsilon\varepsilon_0} \tag{4}$$

where ε is the relative permittivity of the oxide and ε_0 the vacuum permittivity. By insertion of Eq. (3) into Eq. (4) and integration over the oxide boundaries an expression for the ion current under the influence of space charge is obtained:

$$j_i = \frac{4\varepsilon\varepsilon_0 kT\omega_0\exp\left(-\frac{E_a}{kT}\right)}{qx}\cdot\left\{\cosh\left(\frac{E_0qa}{2kT}\right)-\cosh\left(\frac{E_Sqa}{2kT}\right)\right\} \tag{5}$$

With E_0 and E_S denoting the electric field at the metal/oxide and the plasma/oxide interface respectively. Additionally, using steady state approximation in Eq. (3) leads to a second expression for the ion current:

$$j_i = 2qn_{i0}a\omega_0\exp\left(-\frac{E_a}{kT}\right)\cdot\sinh\left(\frac{E_0qa}{2kT}\right). \tag{6}$$

With n_{i0} denoting the ion concentration at the metal/oxide interface. By combination of Eqs. (5) and (6), E_S can be calculated:

$$E_S = \frac{2kT}{qa}\operatorname{arccosh}\left[\cosh\left(\frac{E_0qa}{2kT}\right)-\frac{q^2n_{i0}ax}{2kT\varepsilon\varepsilon_0}\sinh\left(\frac{E_0qa}{2kT}\right)\right]. \tag{7}$$

As the initial stages of oxide growth were not considered here, E_S approaches zero in the case of a space charge limited ion current:

$$\sinh\left(\frac{E_0qa}{2kT}\right) = \frac{2kT\varepsilon\varepsilon_0}{q^2n_{i0}ax}\left[\cosh\left(\frac{E_0qa}{2kT}\right)-1\right]. \tag{8}$$

The oxide growth rate can be derived, considering that every ion that drifts to the oxide/substrate interface contributes to oxide growth:

$$j_i = qN_0\frac{dx}{dt} \tag{9}$$

where N_0 is the number of oxygen atoms that are incorporated into one unit cell of oxide. Inserting Eqs. (6) and (8) for the ion current a parabolic growth rate is obtained:

$$x_t^2 - x_0^2 = 8\omega_0\exp\left(-\frac{E_a}{kT}\right)\frac{kT\varepsilon\varepsilon_0}{q^2N_0}\left[\cosh\left(\frac{E_0qa}{2kT}\right)-1\right](t-t_0) \tag{10}$$

It should be noted that in the initial stages, a linear growth rate is predicted by the Taylor model, because the electric field at the oxide boundaries can be considered as constant for thin films. Therefore an initial oxide thickness x_0 and the starting time of parabolic growth t_0 are included in Eq. (10). Since titanium has a very high oxygen affinity,