

TEMPERATURE CONTROL OF CRYSTALLINE STATUS AND PHENOMENOLOGICAL MODES

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Abstract. A phenomenological model describing the nonlinear process of the growth of Ti and TiO₂ films on Si or SiO₂ substrates is proposed. It is considered that bound electrons from the Si surface are coupled with energy inferior to that of the electrons in the bulk of the Si substrate. The transition from crystalline to vitreous phase in the deposited films is analyzed based upon the nonlinear theory of phase transitions.

Key words: TiO₂ thin films, crystalline status control, surface functionalization with proteins.

1. INTRODUCTION

It is well known that the molecular modeling study of the adsorption of protein subdomains with unlike secondary structures on the surfaces of ceramic titanium dioxide (TiO₂), forming a passivating film on titanium bio-materials that provides the interface between the bulk metal and the physiological environment [1–2] depends on the deposition structure of this material on the substrate [3] and performance. Using molecular dynamics methods, the authors of Ref. [2] studied the effect of the nanoscale structure of the common TiO₂ polymorphs (rutile, anatase and brookite) on the adsorption of an albumin subdomain and on two connected fibronectin modules containing α -helices and β -sheets. They observed that the larger protein subdomain exhibits, as expected, a stronger adsorption, because of its size, but also due to the fact that the three surfaces behave differently. In particular, brookite shows the weakest adsorption, whereas anatase leads to the strongest intrinsic adsorption, in particular for the fibronectin modules. The physical properties of the TiO₂ structure depend on the matrix-assisted pulsed laser evaporation (MAPLE) thin film deposition parameters and are used to address unresolved research questions that have direct relevance to MAPLE performance [4].

In this paper a special attention is devoted to the titanium films deposited in two phases: crystalline and amorphous, necessary for the controlled adhesion of the

organic molecules. Titanium has been used over the last decades as material for bone-anchored implants. However, there are still cases of implant failure. A possible improvement can be expected by coating implant surface with materials with improved physical proprieties, which can ameliorate the adhesion of the biological coatings using proteins and peptides. Fibronectin is an adhesion molecule from the extracellular matrix and has been widely connected with propriety of the deposited TiO_2 layer [5–7]. Controlling the cellular integrin receptors, fibronectin can form stable connections between the extracellular matrix and cells as function of the non-regularities on the TiO_2 surface. Fibronectin is therefore an interesting material for functional surface modifications. We suggest using not only this effect but the non-regularities of the TiO_2 phase proprieties, as well.

2. NONLINEAR MODEL OF PHASE TRANSITION FROM THE CRYSTALLINE TO AMORPHOUS FILMS AS A FUNCTION OF DEPOSITION TEMPERATURE

In this work we propose a model of the phase transition from the crystalline to amorphous one in the deposition of TiO_2 or Ti onto Si or SiO_2 substrate. It is supposed that the electrons on the Si surface are coupled due to existence of voids in the crystalline continuity and have a smaller coupling energy than the electrons forming covalent bonds between Si atoms of the crystalline substrate (Fig. 1). Correspondingly, the coupled energy can be easily dropped by the Ti atoms relaxing on this surface. When the TiO_2 radicals get closer to surface, the unpaired electrons can break the weak coupled pairs of electrons from the surface bounds so that Si crystalline lattice is growing with Ti material. This is possible due to the fact that the coupled electrons to the substrate surface of Si reach a more stable state when entering into a new electronic bond (covalent or ionic) with TiO_2 . Thus, the surface starts to be arranged as a new crystal lattice of TiO_2 . Let's assume that each atom of Ti forms chemical bonds with atoms from Si surface.

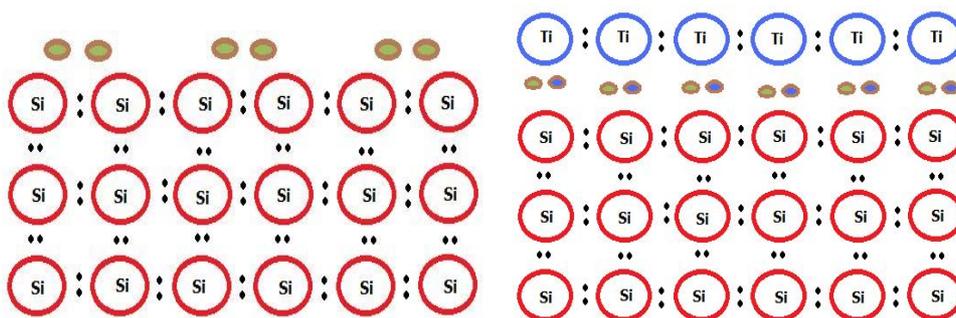


Fig. 1 – Chemical bounding in Si and Si-Ti systems. Electronic couples of Si substrate are represented by dark points. The electrons at the interface forming weak coupling are represented by green dots. The Ti atoms close to surface break those ties creating a continuously growing crystalline network.

Let us represent the stable chemical bonds between the α -atoms by the crystalline harmonic potential

$$V = \sum_{\alpha} \frac{k(x_{\alpha}^0 - x_{\alpha})^2}{2}, \quad (1)$$

where x_{α}^0 is the equilibrium position of the α -atom of Si placed on surface coupled with the Ti atom, while $x_{\alpha}^0 - x_{\alpha}$ is a deviation from the equilibrium position of the Ti atom which enters into the chemical bond with the α Si atom. This multi-hole potential represents the stable crystalline bounds between the Ti and Si atoms and is described by a parabolic function of N variables. When increasing the temperature, the collective oscillations of Ti atoms on the surface bounds become non-harmonic. In excess of a critical temperature, the crystalline arrangement of the atoms on the Si inner surface becomes unstable. As a rule, beginning with this temperature, the collective potential in Eq. (1) has the big number of other non regular equilibrium states, characteristic to the non-crystalline deposition on the TiO₂ substrate.

We analyzed the connection of nonlinear parameters which must be introduced in the potential and the thermodynamic characteristics of the material when increasing of the temperature till non-crystalline phase: critical temperature, heat capacity sound velocity. After inferring this dependence, one can construct the phenomenological potential of the material for which, in the critical points, a transition takes place to the random non-periodical potential of the deposited material. The simplest non-linear potential with two minima can be inferred by decomposing the interaction energy at the position displacement of α Ti atom till the third order of the square value of this deviation from the equilibrium position, $u_{\alpha} = x_{\alpha}^0 - x_{\alpha}$. Here x_{α}^0 is the equilibrium position of the α -atom and x_{α} is the position of α Ti atom.

$$V = \sum_{\alpha} \frac{k(x_{\alpha}^0 - x_{\alpha})^2}{2} - \sum_{\alpha} \beta (x_{\alpha}^0 - x_{\alpha})^4 + \sum_{\alpha} \gamma (x_{\alpha}^0 - x_{\alpha})^6. \quad (2)$$

Here α , β and γ are the constants of the non-Harmonic potential. These constants should be determined from the experiments where is studied the transition from the crystalline to amorphous phases of the deposited material when increasing the temperature.

In order to simplify this approach, one may refer to only one center in the material described by the potential energy

$$V(x_\alpha^0 - x_\alpha) = \frac{k(x_\alpha^0 - x_\alpha)^2}{2} - \beta(x_\alpha^0 - x_\alpha)^4 + \gamma(x_\alpha^0 - x_\alpha)^6. \quad (3)$$

Here, the harmonic constant k describes the crystalline phase of the deposited material on the substrate and can be determined by the dispersion law of the acoustic vibrations on the interface between the Si and Ti: $\Omega(q) = a\sqrt{k/m}|q|t$, a is the lattice constant, m is the reduced mass between the Si and Ti atoms after the process of the first layered position $\mu = \frac{(m_{Ti} + m_{Si})}{m_{Ti}m_{Si}}$, and q is the wave vector of acoustical vibration which is propagated along the surface. For a temperature inferior to the critical one, one can apply the linear dispersion law, so that considering the acoustical frequency $\Omega(q) = v_s|q|$, one can find the connection between the constant k and sound velocity: $v_s = \sqrt{k/m}$.

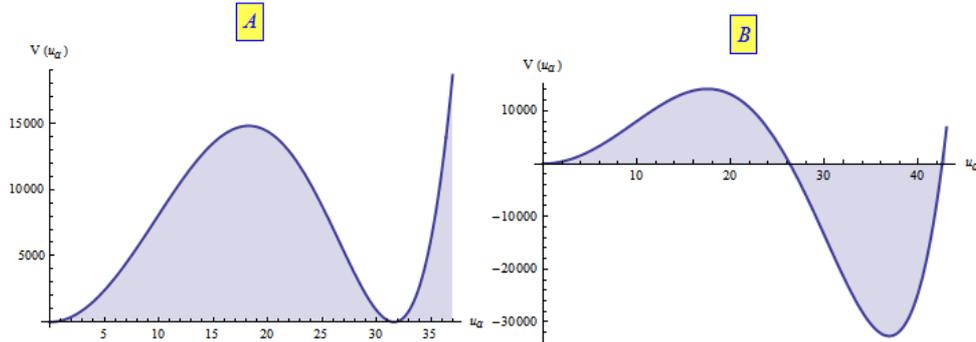


Fig. 2 – Glass minima of non-harmonic potential $V(u)$ for following parameters of the system:
A. $k/2 = 100$, $\beta = 0.2$ and $\gamma = 0.0001$; B. $k/2 = 100$, $\beta = 0.2$ and $\gamma = 0.00008$.

After numerical estimation (Fig. 2), we observed that the potential has two minima for the following values of the system parameters A: $k/2 = 100$, $\beta = 0.2$ and $\gamma = 0.0001$ and B: $k/2 = 100$, $\beta = 0.2$ and $\gamma = 0.00008$. From the analysis of the potential function, it results $V(u_\alpha) = ku_\alpha^2/2 - \beta u_\alpha^4 + \gamma u_\alpha^6$. It follows that this function starting from the zero value of $u^2 = 0$ with increasing of the argument achieves the

maximum value in the point $u_{\max}^2 = \frac{2\beta}{3\gamma} - \sqrt{\left(\frac{2\beta}{3\gamma}\right)^2 - \frac{k}{6\gamma}}$. Then, it decreases till the

point $u_{m2}^2 = \frac{2\beta}{3\gamma} + \sqrt{\left(\frac{2\beta}{3\gamma}\right)^2 - \frac{k}{6\gamma}}$. After reaching the minimum value at the critical point, the non-harmonic potential increases again. We mention that two minima of effective potential exist if the values of the formal parameters β and γ satisfy the inequality $\left(\frac{2\beta}{3\gamma}\right)^2 \geq \frac{k}{6\gamma}$. The second minimum corresponds to the glass deposition of the TiO₂ material on the substrate.

Next, we studied the connection of these parameters with thermodynamic functions of the material near the critical point of phase transition. To this aim, we revised the second order phase transition in the critical point $2\beta = \sqrt{3\gamma k/2}$, starting from which the second “glass” minimum of potential function is possible.

3. CONNECTION OF NON-HARMONIC PARAMETERS OF THE POTENTIAL ENERGY WITH CRITICAL TEMPERATURE OF GLASS DEPOSITION

According to the theory of the second order phase transition, one can find the connection between the parameters β and γ using the decomposition of the thermodynamic potential near the critical point $2\beta = \sqrt{3\gamma k/2}$, where the single hole potential passes in the double holes. Because this effect depends on temperature, it is easy to use near this point the new variable $X^2 = u^2 - u_m^2$. At the critical point $T = T_c$, the maximum and minimum of the double well potential coincide: $u_m^2 = u_{\max}^2 = u_{m2}^2 = \frac{2\beta}{3\gamma}$. Starting with this temperature, the deposition passes from crystalline to vitreous (glass) phases described mathematically by the appearance of the second well of the potential. The model attempts to develop the theory near this critical point, which means to take into consideration only the first and second terms of the potential (3) relative to the new variables X^2 and X^4 . The problem is reduced to the second order phenomenological theory of the phase transition [9]. The thermodynamic potential can be decomposed in similar series near the critical point $T = T_c$:

$$\Phi(T, P, X) = \Phi_0 + A(P, T)X^2 + B(P, T)X^4. \quad (4)$$

Here $\Phi_0 = \frac{ku_m^2}{2} - \beta u_m^4 + \gamma u_m^6$, $A(P, T) = k/2 - 2u_m^2\beta + 3\gamma u_m^4$ and

$B(P, T) = -\beta + 3\gamma u_m^2$. In the Eq. (4) the parameters $A(P, T)$ and $B(P, T)$ were selected according to the second order phase transition theory by Landau [9], while P is the pressure and T is the temperature.

Correspondingly, one can suggest that the parameter $A(P, T)$ don't have singular points close to the phase transition and can be represented as a linear function of the displacement $A(P, T) = a(P)(T - T_c)$ from critical temperature. The coefficient $B(P, T)$ can be approximated by its value in the critical point $B(P, T_c)$. After this approximation, the thermodynamic potential close to the vicinity of the critical point is described by the following temperature dependence $B(P, T_c)$:

$$\Phi(T, P, X) = \Phi_0 + a(P)(T - T_c)X^2 + B(P, T_c)X^4. \quad (5)$$

One notices that under this approximation, the parameter $B(P, T_c)$ can be related to the critical point of the double hole potential $B(P, T_c) = -\beta_c + 2\beta_c > 0$. Close to the vicinity of the second order phase transition, the critical temperature is described by the extremes of the function $\partial\Phi(T, P, X)/\partial X = 0$. For these extremes one gets that $X_m^2 = a(T_c - T)/2B$. By neglecting the higher order

decompositions on the new function X^2 , $S = -\left[\frac{\partial\Phi}{\partial T}\right]_p = S_0 + \left[\frac{\partial A}{\partial T}\right]_p X^2$, we can

obtain the following expression for the entropy: $S = S_0 + \frac{a^2}{2B}(T_c - T)$.

In a similar way, one can obtain the following expression of specific heat capacity of the deposited material:

$$C_p = T \left[\frac{\partial S}{\partial T} \right]_p = C_{p0} - \theta(T - T_c) \frac{a^2}{2B}.$$

Assuming that the parameter k (defined in the last section) does not depend on temperature, we obtain that the entropy can be connected with the critical points

of double hole potential: $S = S_0 - \frac{\partial\beta}{\partial T} u^4$.

From the specific heat capacity jump at critical point, $2\beta = \sqrt{3\gamma k/2}$, one can infer the parameters γ_c and β_c . It is supposed that $B = \beta$. One notices the dependence of the coefficient a^2 on the γ and β non-harmonic parameters. For this we can use the equation

$$A = k/2 - 2u_m^2\beta + 3\gamma u_m^4 = a(T_c - T), \quad (6)$$

where u_{m2}^2 and u_{\max}^2 are the solutions of the equation $k/2 - 2u_m^2\beta + 3\gamma u_m^4 = 0$. According to the Viet theorem, this expression can be factorized as follows: $k/2 - 2u_m^2\beta + 3\gamma u_m^4 = 3\gamma(u_m^2 - u_{m2}^2)(u_m^2 - u_{\max}^2)$. This factorization provides the possibility to find the equation

$$\left(\frac{2\beta}{3\gamma}\right)^2 - \frac{k}{6\gamma} = -\frac{a(T_c - T)}{3\gamma}. \quad (7)$$

Indeed, based upon the critical temperature and the jump of the specific heat capacity, $C_p - C_{p0}$, one can assume that $\beta = \beta_0 T$, so that the Eq. 7 becomes more simple:

$$\left(\frac{2\beta_0}{3\gamma}\right)^2 (T^2 - T_c^2) = \frac{a(T - T_c)}{3\gamma}, \quad (8)$$

where $T_c^2 = \frac{3\gamma k}{8\beta_0^2}$. One can next estimate the value of the parameter γ :

$$\left(\frac{2\beta_0}{3\gamma}\right)^2 (T + T_c) = \frac{a}{3\gamma}. \text{ When supposing } T = T_c, \beta_0 = \beta_0 T \text{ and } \gamma = \gamma_c, \text{ one obtains}$$

$$\gamma_c = \frac{8\beta_c^2}{3aT_c}, \beta_c^2 = \frac{3\gamma k}{8}, \text{ and } T_c^2 = \frac{3\gamma k}{8\beta_0^2}.$$

The phenomenological approach allows finding the connection between experimental observations and theoretical predictions. For example, the distance between first and the second minima of double hole potential can be related to the mean size of the disorder in glasses phase deposition of the TiO₂ material on Si or SiO₂ substrates. By extrapolation and introducing the temperature T instead of T_c , one can find the temperature dependence of the phenomenological parameters, in a larger temperature interval.

4. CONCLUSIONS

We propose a phenomenological model of transition from crystalline to amorphous deposition of the TiO₂ material on Si substrates. We defined the non-harmonic potential function for the vibration of each Ti atom around the equilibrium position. Starting with a specific value of phenomenological parameters of this potential, the system passes from crystalline to glass growth. These parameters are connected to the temperature and thermodynamic functions characteristic to involved materials. The connection of these parameters to the entropy, heat capacity, critical temperature and sound velocity were studied. Our approach permits to construct the phenomenological potential in the glass deposition which can be applied to the estimation of the mean size of the disorders in the glass forming in the growing material. The theory allows for the construction of the potential function $V(u)$, which when increasing the temperature becomes double hole potential. This second hole becomes random for each Ti atom of growing materials. However, under this situation, it is possible to statistically average the double hole potential and find the new connection between the theoretical model and the experimental data.

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