TEMPERATURE RISE OF FILM CONDENSATION SUR-FACE AS A PHENOMENON INTRINSIC TO VACUUM DEPOSITION METHODS

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ABSTRACT

By means of *in situ* measurement of the temperature of condensation surface by two independent methods during deposition of various materials by magnetron sputtering it was revealed that it is noticeably higher than that of the substrate and linearly increases with increasing of the deposition rate of the film. This effect is explained by the idea that intermediate liquid-like layer forms on the boundary between the vapor and solid (film) phases, that exists exceptionally during arrival of sputtered species on the condensation surface. Calculations based on the experimental results show that thermal conductivity of the layer is 8-10 orders of magnitude lower than that for bulk materials. The existence of a layer with such thermal properties provides observing temperature difference between condensation surface and substrate. The suggested simple quantitative film growth model is in a good agreement with experimental results and is invariant relative the film deposition technique.

Key words: surface temperature, calorimetry, magnetron sputtering, growth model, Cr, Cu, Ti, TiN

INTRODUCTION

During film deposition at least two different temperatures can exist: conventional substrate temperature, Ts, which is close to the temperature of a solid film, $T_F \geq Ts$, and the temperature of the growth surface, T_{surf}, which is higher than that of the film, $T_{surf} > T_F$ [1,2]. Clearly, the last one can exist only during the film growth. The reason for the difference between the *surface* temperature and the temperature of already crystallized film can be really existing physical phenomenon [3].

There are few reasons for temperature rise during condensation of atoms: (i) an exothermic release of heat of condensation, ΔH, (ii) kinetic energy of *sputtered* atoms, E_k, during magnetron sputtering, which is one-two orders of magnitude higher compared with that of evaporated atoms, (iii) during magnetron sputtering the growing film is additionally bombarded with ions and fast neutrals that delivers additional heat flux [4]. The sum of these heat fluxes at

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the condensation surface results in high temperature rise at the surface during film growth [5]. Thus it is clear that *real* temperature at which film forms does not equal to conventional substrate temperature which is accepted as a growth temperature. Therefore the information about *real* temperature and its connection with deposition parameters is a key parameter for governing of the film properties and understanding the mechanisms of its growth.

The aims of this work are *in situ* monitoring of the surface temperature T_{surf}, arising during magnetron sputtering of various metals, and creation of a model of film formation based on the obtained results.

EXPERIMENTAL DETAILS

The temperature of a condensation (growth) surface, T_{surf}, during film deposition has been monitored by two principally different methods. The first is based on registration of a heat flux irradiated from a condensation surface during film deposition using high resolution IR-camera along with simultaneous measurement of a substrate temperature by means of thermocouple, for details see [5]. Another one, which is called *calorimetric*, is based on monitoring of temperature–time dependence $T(t)$ (T – measuring temperature, t – time of deposition) for a sample (0.15 mm thick, $\varnothing40$ mm copper disc) suspended on a thin chromel-alumel thermocouple for several deposition rates.

Calorimetric method is based on the following consideration. The temperature of a sample subjected to any type of energetic irradiation increases. When it is yet so low that the heat irradiation is negligible, the influx of energy q_{in} to the sample is

$$q_{in} = m \cdot c \cdot S^{-1} \cdot \frac{\Delta T}{\Delta t} \qquad (1)$$

where $m, c, S, \Delta T/\Delta t$ – are the mass, specific heat, sample's square and rate of temperature change, respectively. If the sample subjected to usual IR-irradiation is a flat plate thin enough that the irradiation from its lateral sides is negligible then the fluxes irradiated from both face sides are equal and the heat outflux q_r irradiated from the sample is described by the Stephen-Boltzmann equation

$$q_r = 2\sigma \cdot \varepsilon \cdot (T_S^{\,4} - T_0^{\,4}) \qquad (2)$$

where σ is Stephen-Boltzmann constant, ε - emissivity of the sample, T_S its temperature, and T_0 is a temperature of environment. It should be highlighted that the multiplier "2" in Eq. (2) indicates the equivalence of the outfluxes from both sides of the sample.

When the temperature reaches maximum then q_r becomes equal to the q_{in}, provided that the heat does not leak away by any other mechanism (*fig.1a*):

$$q_{in} = q_r \qquad (3)$$

If by any reason the outfluxes from the sample's sides are not equal the temperature of the side with lower outflux will be lower than that of the opposite one (*fig.1b*). In this case

$$q_{r0} = q_{r1} + q_{r2} = \sigma \cdot \varepsilon \cdot [(T_1^4 - T_0^4) + (T_2^4 - T_0^4)] \qquad (4)$$

where q_{r0} is the total heat flux irradiated from the sample, q_{r1}, q_{r2} are the outfluxes and T_1, T_2 — the temperatures of the sample sides respectively.
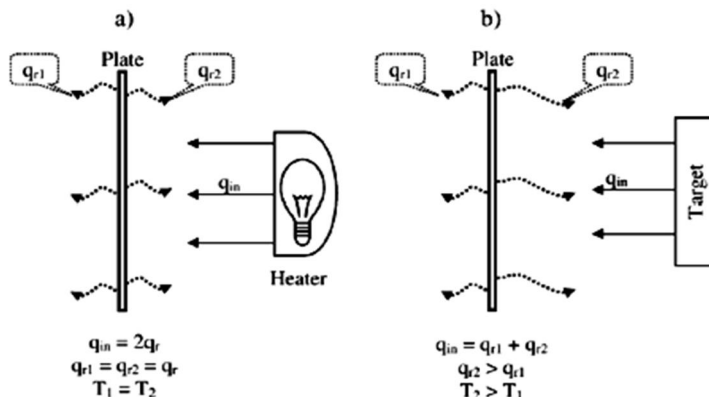

Fig.1 – Scheme demonstrating physical idea of the calorimetric method for determination of the surface temperature. The heat fluxes irradiated from the plate sides under the influence of different heat sources can be: a) equal; b) not equal.

To satisfy the Eq. (4) emissivity ε must be equal for both sides that was achieved by pre-coating of both sides of the sample with the respective material, which was measured by specially developed method. Measuring the temperature T_1 by the thermocouple fixed to the sample, and calculating the influx q_{in} from Eq. (1) we find the other sample's side temperature T_2.

RESULTS AND DISCUSSION

Measurements of the T_{surf} by two independent methods for various materials (Cr, Cu, Ti, Mo, TiN) have shown that: (i) the inequation $T_{surf} > T_S$ holds for all deposited materials; (ii) the T_{surf} and T_S increase linearly with increasing the energy flux, q_{in}, at the substrate, which is proportional to film deposition rate (*fig.2a, b*). Note that the results of measurements by both methods are in accordance.

Big difference between the substrate (T_S) and surface (T_{surf}) temperatures indicates to extremely low thermal conductivity of the substance localized between the vapor phase and the substrate. Crystallized metal film cannot possess such a low thermal conductivity. To realize this effect let us consider the *growing* film as a substance consisting of two different components (*fig.3a*):

(1) very thin surface layer between vapor phase and solid film, which is formed of mobile atoms arriving from a vapor on the growth surface. Due to structureless nature and high mobility of atoms within the layer it can be considered as a *liquid-like* with T_{surf} temperature; (2) solid film under the layer. Whereas thermo-physical properties of a solid film and a substrate keep constant during deposition the thermo-physical properties of a liquid-like layer are unknown and can substantially differ from those for the film and substrate.
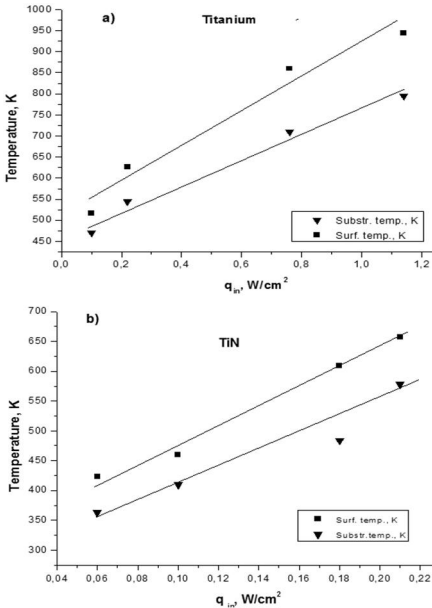

Fig.2 – Calorimetric measurements. The T_S, and T_{surf} temperatures as a function of energy flux, q_{in} during deposition of: (a) Ti and (b) TiN, by magnetron sputtering

The hypothesis about the existence of a liquid-like layer separating the vapor and solid (crystallized film) phases is based on the Ostwald ripening rule. The rule says that the transition of a system unstable at a given conditions (pressure, temperature) to the stable state occurs throw a number of intermediate unstable states [6]. The intermediate state for *vapor→solid* transition is a liquid phase. That is, in accordance with the Ostwald rule the formation of a solid film from a vapor phase should occur throw formation of an intermediate liquid phase – *vapor→liquid→solid* (*v→l→s*). Mechanism of phase transition from vapor to solid throw formation of an intermediate liquid phase during vapor condensation has been suggested in [7] while the experimental confirmation of this mechanism has been obtained later on by Palatnik et al during deposition of films of various materials. They have demonstrated that the film grows by *v→l→s* mechanism at $T_S/T_m \geq 2/3$, where T_m is a melting point of a film material [8]. Liquid-like coalescence of islands during island stage of film growth, which yet has not convincing explanation, also can be explained using model of a liquid-like layer. Observations of the growing metal films by TEM on island stage revealed that islands behave like liquid droplets.

They migrate over a substrate and coalesce like liquid drops while electron diffraction shows their crystalline nature [9]. This behavior can be easily understood if one suggests that the island is composed of already crystallized core coated with a liquid layer (*fig.3b*).
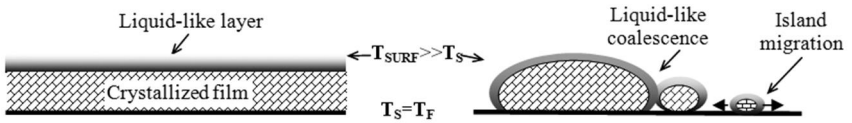
Fig.3 – Scheme demonstrating formation of a liquid-like surface layer at various stages of film growth

Obviously the temperature of the liquid-like layer noticeably higher than that of the underlying solid film, moreover it is nonuniformly distributed along its thickness. Actually, since atoms arriving at the surface possess maximal energy and mobility the upper part of the layer must have maximal temperature. It can result in re-evaporation of part of these atoms, which fraction may reach ~20 % [10]. On the contrary, fraction of the liquid-like layer adjacent to the solidified film consists of atoms, which partially lost their energy and thus possess lower mobility. Therefore, the temperature of this layer's fraction is lower than that of its upper part. Nonetheless, the mobility of atoms in this part of the layer is higher than the vibrational amplitude of the atoms in solid film beneath.

Such model is approved both by theoretical and experimental investigations of the state of atoms on the solid surfaces. Thus, it is shown that even at room temperature normal component of vibrational effective amplitude of the surface atoms two times while tangential amplitude ~30% is larger than that of internal atoms. At that the amplitude quickly decays in deeper atomic layers and in the fifth one beneath the surface has almost the same value as for atoms inside the solid [11].

Formation of a liquid layer during condensation is a process reversal to that of a surface melting occurring during heating of a solid. The description of this process given in [12] says: "As the temperature of solid increases, the atoms acquire additional thermal energy and vibrate with bigger amplitude. The surface atoms are more loosely bound than in the bulk so that their vibrational amplitude is greater. At some higher temperature the surface atoms leave their sites and small fraction of these may escape from the surface as vapor. Others climb out of their sites producing "roughening" on an atomic scale. At this stage the surface layer is mobile and may be considered as a liquid while the bulk still remains solid. The second layer is bound to the underlying solid and to the mobile layer above it. It is thus less strongly anchored to its site than atoms deep in the bulk". That is, the melting of a solid starts from formation of an intermediate liquid-like substance on its surface.

Such model of a surface melting has been experimentally confirmed in recent TEM investigations of melting process of nano-particles of various metals. Thus it has been shown that the melting of the particles starts from for-

mation of a liquid layer on their surface while their core keeps solid up to a temperature some lower than the melting point of a metal [13-15].

Clearly that our reasoning concerning the formation of a liquid layer on the condensation surface and argumentation concerning surface melting are in agreement with Ostwald rule about existing of intermediate states between initial and final stable states. The only difference between these processes consists in their directions – the surface melting occurs in direction while the condensation occurs in the opposite direction, i.e, $v \rightarrow l \rightarrow s$. Mention that up-to-date HRTEM *in situ* investigations demonstrated that transition from unstable amorphous to stable crystalline state occurs throw a number of intermediate states that is one else direct confirmation of the Ostwald ripening rule [16].

Let us now evaluate the thermal resistance of a liquid layer from our experiments using measured T_{surf}, T_S, q_{in} and q_r, and the Eq (5) [17]:

$$R_{tr} = \frac{T_{surf} - T_S}{q_{in} - q_r} \tag{5}$$

On the other hand, the thermal resistance can be expressed as:

$$R_{tr} = \frac{h}{kS} \tag{6}$$

where κ – specific thermal conductivity, h and S – thickness and square of the layer. Substituting experimental values in Eqs (5,6) and taking $h \sim$2-4 nm we obtain specific thermal conductivity of the liquid layer for Cr case $\kappa_l \approx 10^{-8}$ W/m K. Specific thermal conductivity of bulk Cr is κ_{Cr}=94 W/m K. This means that the thermal conductivity of the layer is negligibly small compared with bulk Cr – $\kappa_l / \kappa_{Cr} \approx 10^{-10}$. In view of such low conductivity the heat transfer across the layer is very limited. Just this property of the layer provides its higher temperature compared with the temperature of the film and substrate beneath.

Thermal conductivity of the liquid layer can be also evaluated with the aid of our model [5]. Since atoms in the layer are bonded to each other with metallic bonds, the layer consists of electron and ion subsystems, the ion subsystem is immersed in electron one. The energy exchange within each subsystem is very rapid. At the same time, the energy exchange between different subsystems is very limited. This is a result of a giant difference in the mass of the ions (atoms) and electrons.

Therefore, the main part of the energy stored in the layer is accumulated within the ion subsystem. This assertion is based on the following reasoning. Inside the layer an average velocity of ions $v_i = v_a = (2E_a/m_a)^{1/2}$; here E_a, m_a and v_a are the energy, the mass and velocity of atoms arriving on condensation surface, respectively. The average velocity v_e of electrons is the same as that of ions because prior to condensation and formation of the electron subsystem within the layer all electrons were coupled to incident atoms, i.e., $v_e = v_i = v_a$.

Since $E_i=E_a=1/2[m_a\cdot(v_a)^2]$ and $E_e=1/2[m_e\cdot(v_e)^2]$ and $m_e\ll m_a$ we obtain that $E_e\ll E_i$; here E_e and E_i are the average kinetic energy of electrons and ions, respectively, and m_e is the mass of electron. At the same time, the transmittance of energy of the ion subsystem to the electron one is strongly reduced due to $m_e\ll m_a$. Thus, the main part of energy q_{in} delivered to the growing film and stored in the layer is accumulated within the ion subsystem. The energy of the electron subsystem rapidly equilibrates with that of electrons in a solid film beneath due to a higher mobility of electrons. Therefore, the thermal conductivity of the layer is determined by the thermal conductivity of the ion subsystem and can be estimated as follows.

Thermal conductivity k_{Me} of metals is mostly determined by electrons and from the conventional kinetic theory is expressed by the equation:

$$k_{Me} = \lambda_e\cdot c_{Me}\cdot v_e/3 \qquad (7)$$

Here, λ_e and v_e are the mean free path and the average velocity of electrons in metals respectively, and c_{Me} is the specific heat of metal. Since the heat of the layer is accumulated within its ion subsystem, the thermal conductivity k_l of the layer is determined by the ion subsystem. Therefore, to estimate the thermal conductivity k_l in Eq. (7) we must replace λ_e with λ_a and v_e with v_a. Then the k_l is defined as $k_l=\lambda_a\cdot c_{Me}\cdot v_a\cdot(m_e/m_a)/3$; the ratio m_e/m_a is the factor determining the decrease in the energy transfer from ions to electrons. Assuming that the specific heat of the layer is equal to that of the bulk metal we obtain the ratio of thermal conductivities of the layer to that of metal:

$$k_l / k_{Me} \approx (\lambda_a/\lambda_e)\cdot(v_a/v_e)\cdot(m_e/m_a) \qquad (8)$$

To estimate of k_l for Cr we must substitute in Eq. (8) $m_e/m_{Cr}\approx1.1\cdot10^{-5}$, $\lambda_a/\lambda_e\approx5\cdot10^{-3}$ and $v_a/v_e=(m_e/m_{Cr})^{1/2}=3.28\cdot10^{-3}$. After substitution of $\lambda_a\approx0.2$ nm (average interatomic distance in liquid) and $\lambda_e\approx40$ nm we obtain $k_l\approx10^{-10}\cdot k_{Me}$. This means that the effective thermal conductivity of the liquid layer formed during growth of chromium film is ten orders of magnitude lower than that conventional thermal conductivity of bulk chromium. To estimate how properties of the depositing element influence the thermal conductivity of the layer one should substitute the mass of the corresponding element to Eq. (8). Doing this for the light carbon and heavy tungsten we find that k_l ot these elements varies from $\sim10^{-9}$ to $\sim10^{-11}$. This means that the effective thermal conductivity of the layer is very low and slightly depends on the sputtered material.

The above consideration shows that the model does not anchor to the film deposition method and thus is universal. Actually, from fig.2 it is seen that the T_{surf} depends exceptionally on the *energy* flux delivered to the substrate by film-forming species and other particles taking part in the deposition process. In other words, the liquid-like layer will form during deposition of a film by *any* technique. It's quite another matter, that thickness and temperature of the layer will depend on the deposition technique. Actually, both of these parame-

ters are functions of the flux of energy depositing to the substrate that varies in orders of magnitude depending on the deposition method. Obviously just the latter circumstance as well as methods for temperature measurement did not allow to reveal a big difference $\Delta T = T_{surf} - T_S$ in previous investigations.

CONCLUSIONS

The temperature of the condensation surface measured *in situ* by two independent techniques during deposition of various materials by magnetron sputtering is shown to be substantially higher than that of the substrate and linearly increases with increasing of the growth rate of the film. This phenomenon is explained by the idea of formation of an intermediate liquid-like layer that forms on the boundary between the vapor and solid (film) phases. The thermal conductivity of the layer is 8-10 orders of magnitude lower than that for bulk materials and exists exceptionally during arrival of sputtered species on the condensation surface. The existence of a layer with such thermal properties provides observing temperature difference between surface and substrate. The suggested film growth model is invariant relative the film deposition technique.

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