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The correlation between film structure and surface temperature

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The structure of metal films deposited from fluxes of energetic and thermalized sputtered atoms has been studied in detail. The growth surface temperature T_{surf} developing during the condensation of sputtered atoms has been measured by two independent techniques.Variations in the film structure from fine-grained in the interface region to coarse-grained in the upper part of the film correlate with variations in the T_{surf} . The T_{surf} being equal to the substrate temperature at the beginning of the deposition steeply increases and remains several times higher than the substrate temperature during the process. We explain this effect by formation of a liquid-like layerwith low thermal conductivity that forms on the growth surface during deposition. Due to this layer we assert that the film grows by a "gas→liquid→solid" rather than a "gas→solid" mechanism independently on the deposition method.

Исследована структура металлических пленок, осажденных из потоков энергетических и термализованных распыленных атомов. Двумя независимыми методами измерена температура поверхности роста T_{surf}, возникающая в процессе конденсации атомов. Изменения структуры от дисперсной в приподложечной области до крупнозернистой в верхних частях пленки коррелируют с изменениями T_{surf} в процессе роста пленки. T_{surf}, будучи в начале процесса равной температуре подложки T_S, быстро растет и, достигнув определенной величины, остается в несколько раз больше T_S на протяжении всего процесса. Этот эффект объяснен образованием на поверхности роста в процессе формирования пленки жидкоподобного слоя с низкой теплопроводностью. Существование такого слоя позволяет утверждать, что пленка растет по механизму "пар→жидкость→кристалл", а не "пар→кристалл", независимо от метода осаждения.

Films deposited by plasma-based methods grow from fluxes of particles with increased kinetic energy. Contemporary growth theories developed for such films mainly focus on collision-induced effects produced by energetic species on the growth surface. At the same time, most of the energy losses by such species during condensation are realized as heat [1]. Therefore one can expect that the realeasing heat increases surface (growth) temperature T_{surf} and thus might considerably affect the film structure. Whereas the development of high T_{surf} noticeably exceeding substrate temperature T_S during film deposition [2–5] has been reported, there are no works exploring the correlation between the film structure and the T_{surf}. In this paper, we present the results of investigation of the structure of chromium films deposited by magnetron sputtering from fluxes of energetic and thermalized atoms along with the results of measurements of the T_{surf} developed during condensation of sputtered atoms. Strong correlation between the film structure changes along thickness and variations in

the T_{surf} during deposition is revealed. A model explaining this effect is presented.

The experimental details of the film deposition by magnetron sputtering technique are presented elsewhere [5]. The magnetron was equipped with 4 mm thick Cr, Ti, Cu or Mo (99.99) target of 50 mm in diameter bonded with Ag paste to the cooled Cu backing plate. The background argon pressure was $p_0 = (1-3)\cdot 10^{-3}$ Pa whereas the operating pressures were $p_{Ar} = 0.2$ and 5 Pa (low and high pressure conditions, respectively). The high pressure conditions provided the film deposition from fully thermalized atoms while the films grown at low pressure were deposited from high-energy atomic fluxes. The flux of sputtered atoms (deposition rate) was regulated by variation of the discharge current.

The T_{surf} was measured by two independent methods. In the first method the T_{surf} was measured by means of VARIOSCAN High Resolution Thermography System (JENOPTIC Laser, Optic System GmbH) with post processing of thermograms recorded during deposition using the IRBIS Professional software. Temperature measurements within the range from -40 to $+1200$°C with the accuracy ±1 % of the full-scale value were carried out by comparing the radiation intensity of the heated object and reference source mounted inside the IR camera. A ZnSe window, transparent in IR region (6–20 μm), served as a viewport for the IR camera. Silicon plates precoated with 1500 nm thick Cr, Ti or Cu coatings were used as substrates. The coatings were prepared to be sure that the emittance ε of the depositing film is equal to the ε of the substrate that substantially increased the accuracy of the surface temperature determination. The substrates were tightly attached to the cooling substrate holder that provided the substrate temperature T_S to be in the range of 18–20°C during the whole process. The chromel-alumel thermocouple fixed to the substrate was used to measure the T_S.

Another method for the T_{surf} measurements was developed for the first time and 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 $q_{in} = m \cdot c \cdot S^{-1} \cdot \Delta T/\Delta t$. When the temperature reaches maximum at a given q_{in} the heat outflux $q_r = 2\sigma \cdot \varepsilon \cdot (T_S{}^4 - T_0{}^4)$ irradiated from the sample becomes equal to the q_{in}, provided that the heat does not leak away by any other mechanism, i.e., $q_{in} = q_r$. The values in the Eqs are as follows: ΔT/Δt is a temporal temperature dependence taken from a linear part of the heating curve, m - mass, c - specific heat, S - surface area of the sample,(sigma) - Stefan-Boltzmann constant, TS - temperature of the sample at an equilibrium state, and T0 temperature in the chamber.If by any reason the outfluxes from the plate's sides are not equal the temperature of the side with lower outflux will be lower than that of the other side. In this case $q_{r0} = q_{r1} + q_{r2} = \sigma \cdot \varepsilon \cdot [(T_1{}^4 - T_0{}^4) + (T_2{}^4 - T_0{}^4)]$, where q_{r0} is the total heat flux irradiated from the plate, q_{r1}, q_{r2} are the outfluxes and T_1, T_2 – the temperatures of the plate sides, respectively. To satisfy the latter equation emissivity ε must be equal for both sides what can be achieved by pre-coating of the plate with the respective material. Measuring the temperature T_2 by the thermocouple fixed to the plate, and calculating the influx q_{in} we find the other plate's side temperature T_1.

Based on this reasoning the measurements of the T_{surf} during deposition of Cr, Cu, Ti and Mo films were performed. To establish the relationship between T_{surf} and q_{in} the films were deposited with various deposition rates (q_{in}'s) onto free-hanging polished copper plates pre-coated with the respective metal. To prevent heat losses due to thermal conductivity the plate was suspended on a thin chromel-alumel thermocouple used for the temperature measurements with the tip fixed to the plate. To compare the effects of atomic condensation and conventional IR radiation the pre-coated plates were subjected to IR irradiation from the incandescent lamp with variable (0–1000 W) power in the chamber filled with Ar at the same pressure. The procedure of measurements and calculations was similar to that used for the film deposition.

The structure of the samples prepared for cross-sectional investigations was studied using selected-area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM). For this purpose, a high-resolution (0.2 nm by point, 300 kV accelerating voltage) JEOL-3010 electron microscope was utilized. Special measures were taken to increase the accuracy of the lattice parameter measured from the SAED data [8]. The analysis of the film composition using an energy dispersive X-ray

spectrometer (energy resolution 138 eV, spatial resolution 10 nm) attached to the S3500H scanning electron microscope confirmed that the films did not contain any impurities other than 1.3–1.5 wt.% of carbon.

Detailed analysis of SAED patterns and micrographs taken from different parts of the film deposited from thermalized atoms shows that the film is crystallized in low-temperature (LT) Cr phase [6], uniform along thickness, and consists of ~90 nm-diameter narrow columns which in turn are formed of 30–50 nm crystallites (Fig. 1). To the contrary, the film deposited from high-energy atomic flux (q_{in} = 0.12 W/cm^2) on a non-heated substrate is crystallized in ordinary high-temperature (HT) Cr phase and is non-uniform along thickness [7], as shown in Fig. 2. The lower part of the film, which spans less than 0.1 of the total film thickness, consists of small round-shaped crystallites of about 6–8 nm (Fig. 2b) while the average crystallite size in the upper part of this film is about 30–40 nm with crystallites elongated and preferentially oriented along the columns (Fig. 2a). At the same time, the film deposited at 500°C is almost uniform along the thickness with the average crystallite size of ~20–30 and 30–40 nm in the lower (Fig. 3b) and upper (Fig. 3a) parts, respectively. The crystallites in the upper part are elongated and preferentially oriented along the columns whereas those in the lower part are more equiaxed and distributed more chaotically. An important feature of the 500°C film is that its lattice constant is equal to that of the upper part

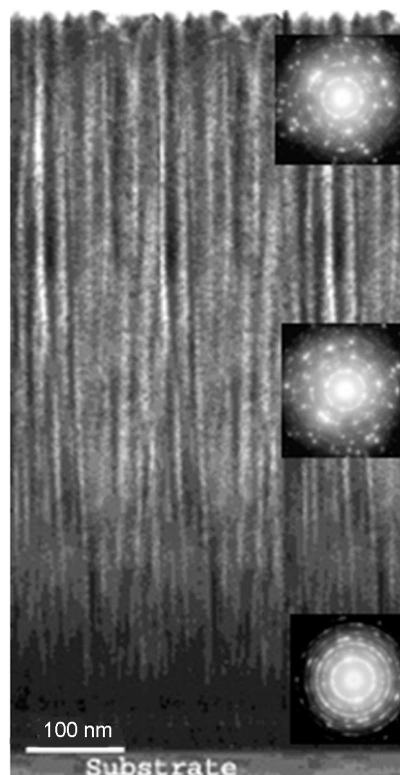

Fig. 1. Cross-sectional view of Cr film deposited at high-pressure conditions. Inserted SAED patterns where taken from the low, middle and top parts of the film. The film thickness is ~5000 nm.

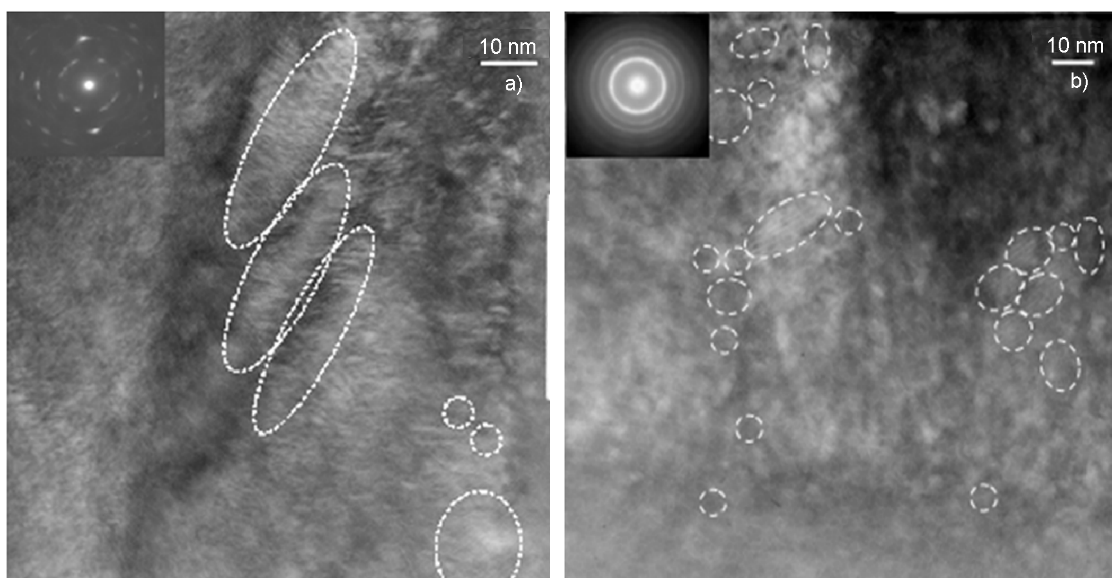

Fig. 2. Cross-sectional views and SAED patterns of (a) the upper, and (b) the lower parts of Cr film deposited on a non-heated Si substrate at low-pressure conditions (q_{in} = 0.12 W/cm^2). The dashed lines show the approximate boundaries of the crystallites. The total film thickness is ~1500 nm.

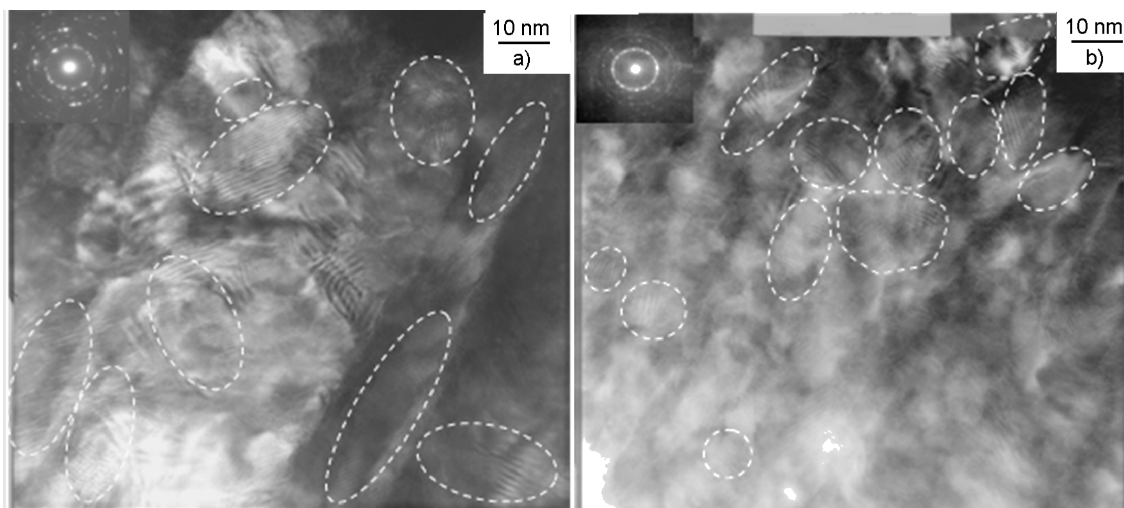

Fig. 3. Cross-sectional views and SAED patterns of (a) the upper, and (b) the lower parts of Cr film deposited on Si substrate (T_S = 500°C) at low-pressure conditions (q_{in} = 0.12 W/cm^2). The dashed lines show the approximate boundaries of the crystallites. The total film thickness is ~1500 nm.

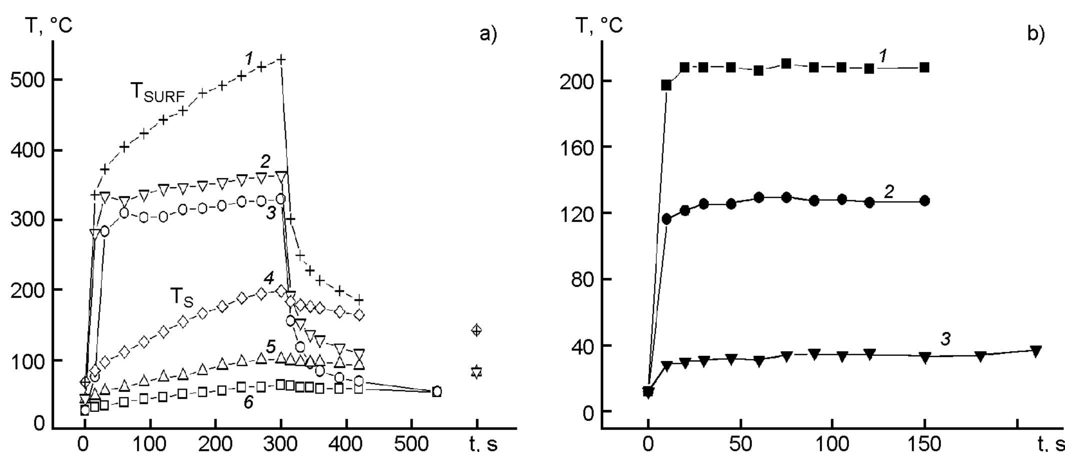

Fig. 4. Measurements by the IR-camera. Time dependences of the T_{surf} and T_S obtained during deposition of Cr on Si: (a) on cooling, *1* – q_{in}= 0.07, *2* – 0.07 , *3* –0.12, *4* – 0.12, *5* – 0.20, *6* – 0.20 W/cm^2, (b) non-cooling substrates, as functions of the *1* – q_{in} = 0.07, *2* – 0.12, *3* – 0.20 W/cm^2. The substrate temperature during deposition on cooling substrate did not exceed ~293 K during measurements.

of the film deposited under the same conditions onto a non-heated substrate [7].

The time dependences of the T_{surf} and T_S measured by the IR-camera during Cr deposition at various flux densities (deposition rates) are presented in Fig. 4. It is seen that the T_{surf} is proportional to the atomic flux density, sharply grows as the condensation is started, does not change under steady-state conditions, and steeply decays after switching the flux off. At the same time, the T_S either changed in the same manner as the T_{surf} for the non-cooling substrate remaining several times lower than the T_{surf} (Fig. 4a), or did not change (for the cooling substrate the $T_S \leq$~20°C for all experiments, Fig. 4b). Similar to these results were obtained by the calorimetric method. Temperature-time dependences $T(t)$ presented in Fig. 5 were recorded during deposition of Ti films at various deposition rates.

The formation of the LT Cr phase in the film deposited from thermalized atoms indicates that the growth temperature during deposition was <400°C [8]. To the contrary, the film deposited from non-thermalized atoms on a non-heated substrate was crystallized in the ordinary HT Cr phase. Since the only factor defining formation of the HT Cr phase is the temperature, it is reasonable to assume that the growth temperature developed during deposition of the film from non-thermalized atoms was >400°C, at which the formation of the LT phase is im-

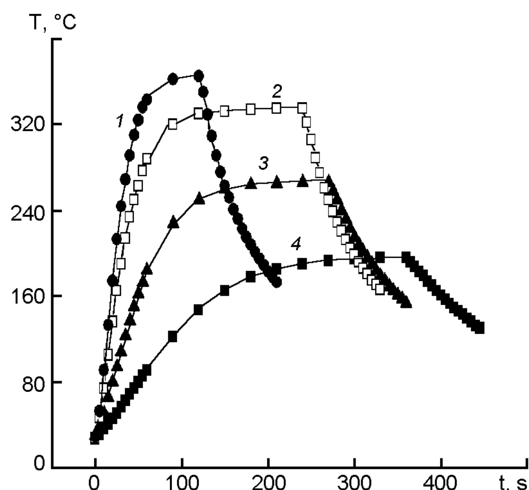

Fig. 5. Calorimetric measurements. Time dependences of the T_{surf} obtained during deposition of Ti on double-side Ti-coated Cu plate, as a function of the q_{in}. The numbers over the plots represent the measured T_S and calculated T_{surf}, respectively.

1 $-T_s$= 365 T, T_{surf} = 542 T, q_{in}= 0.08 W/cm^2;

2 $-T_s$= 335 T, T_{surf} = 489 T, q_{in}= 0.20 W/cm^2;

3 $-T_s$= 266 T, T_{surf} = 357 T, q_{in}= 0.42 W/cm^2;

4 $-T_s$= 196 T, T_{surf} = 217 T, q_{in}= 0.57 W/cm^2.

possible. This assumption is supported by the fact that the lattice parameter of the upper part of the latter film coincides with that of the film deposited at 500°C.

Changes occurring in the microstructure of the film deposited from non-thermalized atoms correlate with the behavior of the time dependence of the T_{surf} (q_{in} = 0.12 W/cm^2). Actually, the part of the film formed at the beginning of the deposition (the part adjacent to the substrate) consists of small crystallites with a defect crystal structure (Fig. 2b) when the T_{surf} is small and close to the T_S (Fig. 4a). The upper part of this film is formed of crystallites with larger size and improved structure (Fig. 1a), which is in accordance with the high T_{surf} developed at the end of the deposition. At the same time, the T_S was ~150°C during growth of this film (Fig. 4a). These observations show that the real growth temperature is the temperature developing on the surface rather than the substrate temperature. The only physical reason for the large temperature difference between the surface and the substrate, i.e., the development of a large temperature gradient across the growing film, is its low thermal conductivity k, which is inversely related to the thermal resistance, $R = 1/k$.

To reveal the reason for the low thermal conductivity (or high thermal resistance) of the growing film, let us consider its physical (not crystal) structure. During the growth the film consists of three fractions: (i) a thin superficial layer, which forms on the growth surface due to condensation of sputtered atoms and consists of mobile adatoms, (ii) a solid film beneath it, and (iii) an interface between the solid film and the substrate. The thermal resistance of such a system is a sum of the resistances of its constituents. The combined thermal resistance of the metal film and the interface, provided that the film intimately adheres to the substrate, is of the order of that of bulk metals, i.e., of the order of thousandths of mKW^{-1}. Therefore the main contribution to the thermal resistance of the growing film is the superficial layer existing during atomic condensation. Taking values of the surface and substrate temperatures, T_{surf} and T_S, from the experiment and calculating the energy flux to the condensation surface, q_{in}, as in [9], we estimate the thermal conductivity of this layer, balancing q_{in} with the heat flux irradiated from the growth surface q_{rad} (calculated from the Stephen-Boltzmann law), and the energy losses q_{tc} due to the thermal conductivity of the layer: $q_{in} = q_{rad} + q_{tc}$. Following the approach developed in [9], q_{tc} is expressed as $q_{tc} = k_l \cdot S \cdot (T_{surf} - T_S)/t$. Assuming a layer thickness on the order of $t \sim 10^{-7}$ m, which is the average thickness at which the surface temperature saturates, we obtain $k_l \sim 10^{-7}$ Wm^{-1}K^{-1}. Comparing this value with that of the bulk chromium we obtain $k_l/k_{bulk} \sim 10^{-9}$. This shows that the thermal conductivity of the layer existing during the condensation is, indeed, negligibly small compared to the bulk metals and becomes close to it after switching the atomic flux off.

Estimation of the thermal conductivity of this layer based on the model developed in [10] shows fairly good agreement between the k_l/k_{bulk} value calculated above. Thus the surface temperature measured by means of the IR-camera during deposition is a temperature of a thin superficial "hot" layer that consists of mobile adatoms and possesses extremely low thermal conductivity. Such a low thermal conductivity is conditioned by the very limited energy exchange between adatoms in the layer and the solidified film beneath. This "hot" layer represents a substance separating the vapor phase from the solid and can be viewed as a hot liquid-like layer.

From the reasoning above it follows that the layer will form on the growth surface at

any deposition conditions. However since its existence can be fixed only by measuring of its temperature, T_{surf}, which depends solely on the flux of energy delivered to the growth surface, q_{in}, for deposition methods with low q_{in}'s the layer will be negligibly small. The latter fact could be a reason why the earlier attempts to measure the T_{surf} for evaporation methods where failed [11].

Based on the results and discussion above we assume that the film deposited from atoms with relatively large kinetic energy grows: (i) under gradual elevation of the surface temperature, T_{surf}; (ii) initial stages of the growth occur at temperature close to the substrate temperature, T_S, while the further growth occurs at $T_{surf}>T_S$ depending on the flux of energy delivered to the growing surface; (iii) the changes in the T_{surf} cause the formation of non-uniform film structure; (iv) the film grows by "vapor→liquid→solid" rather than "vapor→solid" mechanism, where the liquid phase is represented by a superficial liquid-like layer which temperature is considerably higher than the substrate temperature.

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Взаємозв'язок між структурою плівок і температурою, що розвивається на поверхні росту

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Досліджено структуру металевих плівок, осаджених з потоків енергетичних і термалізованих розпорошених атомів. Двома незалежними методами виміряно температуру поверхні росту T_{surf}, яка виникає у процесі конденсації атомів. Зміни структури від дисперсної в області під підкладкою до грубозернистої у верхніх частинах плівки корелюють із змінами T_{surf} у процесі росту плівки. На початку процесу T_{surf} дорівнює температурі підкладки T_S, але швидко зростає і, досягнувши певної величини, залишається у декілька разів більше T_S впродовж всього процесу. Цей ефект пояснено утворенням на поверхні зростання у процесі формування плівки рідкоподібного шару з низькою теплопровідністю. Існування такого шару дозволяє стверджувати, що плівка росте за механізмом "пара→рідина→кристал", а не "пара→кристал", незалежно від методу осадження.