Pis'ma v ZhETF, vol. 83, iss. 3, pp. 143 – 147 © 2006 February 10

Anomalously high surface temperature induced by condensation of atoms

L. R. Shaginyan[+*], *N. V. Britun*[*], *J. G. Han*[*], *V. R. Shaginyan*[△*]

[+]*Institute for Materials Science Problems of National Academy of Sciences of Ukraine, 03142 Kiev, Ukraine*

[*]*Center for Advanced Plasma Surface Technology, SungKyunKwan University 300 Chun-Chun-Dong Jangan-gu Suwon 440-746 Korea*

[△]*Petersburg Nuclear Physics Institute, RAS, 188300 Gatchina, Russia*

Submitted 22 November 2005
Resubmitted 26 December 2005

The effect of extremely high temperatures developing on surface during the condensation of sputtered atoms has been discovered for the first time by direct surface temperature measurements. This temperature is considerably higher than the temperature of solid film beneath and proportional to the flux of atoms impinging on the surface. Surface temperature steeply grows as the condensation starts, exists during the period of condensation and rapidly decays after its stopping. The effect is related to the anomalously low thermal conductivity of superficial layer that is formed by highly mobile atoms arriving on the condensation surface. This superficial layer can be viewed as a new state of matter characterized by its anomalously low thermal conductivity.

PACS: 68.08.–p, 68.55.–a, 68.60.–p

The effect of the temperature rise of the condensation surface of films during condensation of atoms of solids was discussing intensively in 60-s [1]. The base of this effect is the kinetic energy of atoms impinging on the surface and the exothermic release of the heat of condensation due to a vapor-solid transformation. The heat elevates the temperature of the surface (TOS) that is expected to be considerably higher than the temperature of the solid film. Upon using thin film temperature sensors, earlier measurements of the temperature have shown that the effect may really exist [2, 3]. The effect has also been observed during the condensation of evaporated metal atoms by measuring the infrared irradiation from the condensation surface [4]. Later on these results were questioned [5, 6]. Recent studies of TOS using in situ spectroscopic ellipsometry have demonstrated the existence of noticeable (about 100 K) temperature difference between the surface and the substrate during PE CVD (Plasma-Enhanced Chemical Vapor Deposition) of silicon [7] and diamond [8] films. Taking into account the high thermal conductivity of metal films and its thickness, it is impossible to explain this noticeable temperature difference using the common theory of thermal conductivity which could hardly account for the temperature difference as high as 0.1 K. Nonetheless, the effect could arise due to the extremely low thermal conductivity of the film surface. Therefore the detection of the difference between temperatures of the surface and the bulk during atomic condensation may reveal a new physics related to the transport of heat at the surface. Since the temperature of surface has a strong impact on the growth of films, this detection will also clarify the physics of the formation of solid films from the vapor making the study of TOS be crucial point.

In this letter we confirm our recent indirect observations of the effect of high surface temperature developed during deposition of sputtered films [9] by direct in situ measurements of TOS during the condensation of chromium and copper atoms using infrared high-resolution surface thermography system.

The schematic diagram of experimental setup is given in Fig.1. The axes of the magnetron and IR camera intersect at the center of substrate holder located at distance 70 mm from the magnetron generating a flux of metal atoms. ZnSe window transparent in IR region 6–20 μm located at distance 450 mm from the substrate holder serves as a view-port for the IR camera. The magnetron is equipped with 4 mm thick Cr or Cu (99.99) target of 50 mm in diameter bonded with Ag paste to the cooled Cu backing plate. The background pressure $p_0 = (1-3)\cdot 10^{-3}$ Pa and the operating argon pressure $p_{Ar} = 0.3$ Pa. The flux density of sputtered atoms was regulated by variation of the magnetron discharge current I_d. As substrates silicon plates ($20\times 20\times 0.5\,\text{mm}^3$) pre-coated with 1500 nm thick Cr and Cu films were used. This measure was taken to be sure that the emissivity of the depositing film is equal to the emissivity of the substrate that substantially in-

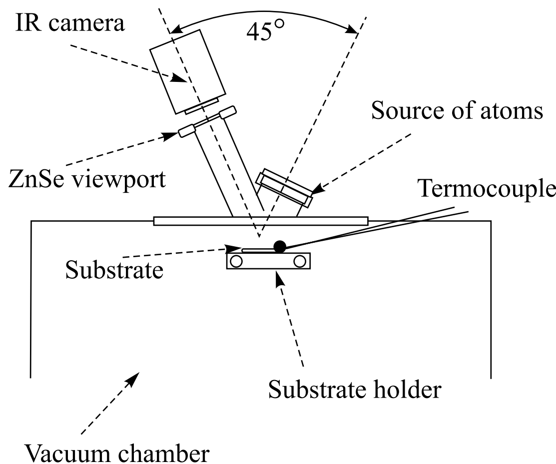

Fig.1. Experimental setup for in situ surface temperature measurement

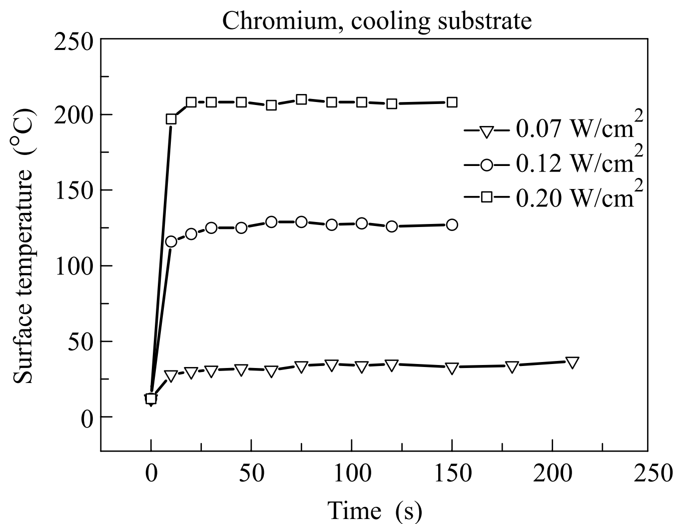

Fig.2. Time dependencies of the surface temperature T_{surf} developed during the condensation of chromium atoms on cooling substrate. Temperature T_{surf} is presented for different values of flux q_{in} shown in the inset

creased the accuracy of the surface temperature determination. The substrates were tightly attached to the substrate holder cooled with a circulating coolant kept at temperature 5–8 °C. The chromel-alumel thermocouple attached to the substrate surface by a spring was used to measure the substrate temperature T_s. The thermocouple was screened by a shield to avoid the direct incidence of sputtered atoms.

TOS was measured by means of "VARIOSCAN High Resolution Thermography System" (JENOPTIK Laser, Optik Systeme GmbH) with post processing of the thermograms by the "IRBISO Professional" software. TOS is determined by the measurement of infrared irradiation $8-12\,\mu$m from the surfaces heated by the flux. Temperature measurements within the range of $-40+1200\,°$C with the accuracy of 1% of full-scale value are made possible by comparing the radiation intensity of the object and the reference source mounted inside the camera. To calibrate the camera, simultaneous temperature measurements of Cr and Cu films preliminary deposited onto Si wafers clamped to the heating holder, by the camera and the thermocouple were performed without deposition. The initial emissivity ε of Cr and Cu was taken from [10]. The discrepancy in camera and thermocouple readings was in limits of $\pm(8-10)\,°$C in the range $25-700\,°$C. Using this method the temperature dependence of $\varepsilon(T) = (0.08-0.1)$ for Cr and $\varepsilon(T) = (0.032 \pm 0.003)$ for Cu films in this temperature range was determined and used in further measurements.

The time dependence of TOS measured by the camera for various values of the flux q_{in} of energy delivered by chromium and copper atoms arriving at the surface are presented in Figures 2 and 3.

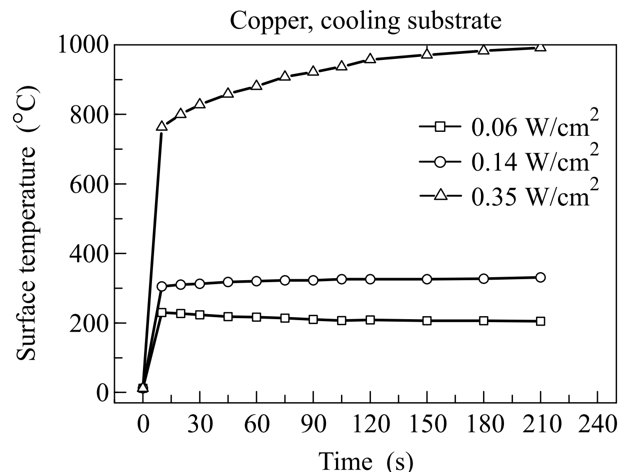

Fig.3. Time dependencies of the surface temperature T_{surf} developed during the condensation of copper atoms on cooling substrate. Different values of flux q_{in} are shown in the inset

These show that the surface temperature is proportional to the flux q_{in} delivered by sputtered atoms, sharply grows as the condensation is started and keeps unchangeable in steady state conditions. While the substrate temperature either did not change (in case of cooling substrate it kept around $15-18\,°$C during deposition) or changed in the same manner as TOS, however, remaining several times lower than TOS for the noncooling substrate as seen from Fig.4. It is also seen from Fig.4 that T_{surf} steeply decays after switching the flux q_{in} off.

The discharge currents and the corresponding deposition rates; the atomic and heat fluxes delivered to the substrate during surface temperature measurements when depositing chromium and copper films

Depositing metal	I_d [A]	Deposition rates [nm/sec]	Atomic flux f_d [atom/cm^2·sec]	Heat flux E_p [W/cm^2]	$D_c + E_k + E_p$ [eV/atom]
Cr	0.2	1.62	$1.4 \cdot 10^{16}$	0.04	20
Cr	0.4	2.64	$2.2 \cdot 10^{16}$	0.07	20
Cr	0.6	4.41	$3.8 \cdot 10^{16}$	0.12	20
Cr	1.0	7.4	$6.3 \cdot 10^{16}$	0.2	20
Cu	0.2	3.1	$2.6 \cdot 10^{16}$	0.06	17
Cu	0.4	6.2	$5.3 \cdot 10^{16}$	0.14	17
Cu	1.0	15.2	$13.0 \cdot 10^{16}$	0.35	17

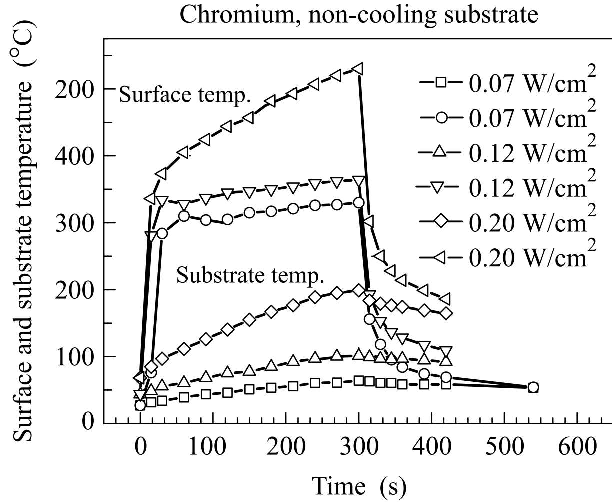

Fig.4. Time dependencies of both the surface temperature and the temperature of the non-cooling substrate developed during condensation of chromium atoms and measured at the different values of the flux q_{in} shown in the inset

The accuracy of the TOS determination in the last case was lower because of the variation of the environmental temperature used in the camera software as an external parameter. Depending on the substrate temperature, the environmental temperature is growing during the condensation in the case of non-cooling substrate that reduces the measurement accuracy.

Therefore when estimating the thermal conductivity, we used the surface temperature values obtained for cooling substrates.

To realize the reasons of the extremely high TOS, we estimated the thermal conductivity of the thin layer appearing on the condensation surface which is formed by mobile atoms arriving on the condensation surface. This was made by consideration of the heat balance on the condensation surface. The flux of energy q_{in} incoming on the condensation surface is [11]

$$q_{\mathrm{in}} = f_d(D_c + E_k + E_p), \tag{1}$$

where f_d(atom/cm^2·sec) is the flux of sputtered atoms calculated from the deposition rate, D_c and E_k are the heat of condensation and average kinetic energy of sputtered atoms, E_p is the heat flux from the plasma, each in eV/atom. These values were taken from [11]. The atomic and heat fluxes calculated from the measured deposition rates of chromium and copper films at the corresponding discharge currents I_d are presented in Table.

According to Stefan-Boltzmann law, the heat flux q_{rad} irradiated from the surface at temperature T_{surf} is

$$q_{\mathrm{rad}} = \sigma\varepsilon[(T_{\mathrm{surf}})^4 - (T_0)^4], \tag{2}$$

where σ is the Stefan-Boltzmann constant, ε is the emissivity, $T_0 = 300$ K is the chamber temperature. Then the difference, $q_{\mathrm{in}} - q_{\mathrm{rad}} = q_{tc}$, is the heat losses due to the thermal conductivity of the layer. The Fourier law adapted for the thermal resistance R_{th} of the layer reads [12]

$$R_{th} = \frac{T_{\mathrm{surf}} - T_{\mathrm{substr}}}{q_{\mathrm{in}} - q_{\mathrm{rad}}}. \tag{3}$$

We define

$$R_{th} = \frac{d_l}{k_l S}, \tag{4}$$

with d_l the layer thickness, k_l its thermal conductivity and S the surface area. Taking T_{surf} and T_{substr} from the experiment and q_{in} calculated from Eq. (1) and assuming the layer thickness of order of $d_l \sim 10^{-7}$ m, the average thickness at which the surface temperature saturates, we obtain $k_l \sim 10^{-7}$ (Wm^{-1}·K^{-1}). Comparing this value with those of the bulk chromium or copper [10], we obtain $k_l/k_{\mathrm{bulk}} \sim 10^{-9}$. This shows that the thermal conductivity of the layer existing during the condensation is negligibly small compared to that of the bulk metals and becomes close to it after switching the flux q_{in} off.

To understand the physics determining this extremely low thermal conductivity, we have to consider

how the growing film is formed. Note that here we consider the usual scheme of film deposition when a film grows on any type of the substrate. In our experiments, the Si substrate was preliminary pre-coated with the corresponding (Cr for condensation of chromium atoms etc.) metal layer. During the condensation as it is shown in Fig.5, the film consists of three fractions: the liquid-like hot thin layer appearing on the surface and formed by mobile atoms from the vapor, the solid growing film beneath it, and the interface between the film and the substrate. Therefore, the thermal resistance of the film is the sum of the resistances of these constituents. The thermal conductivity of metal films is poorly investigated. Continuous metal films possess electrical resistivity close to bulk metals [13]. Due to the Wiedemann-Franz law, we expect their thermal conductivity to be of the order of bulk metals. The thermal conductivity of the interface is also high, provided that the metal film intimately adhering to the substrate [14]. Thus, only the superficial layer appearing during the atomic condensation contributes to the thermal resistance.

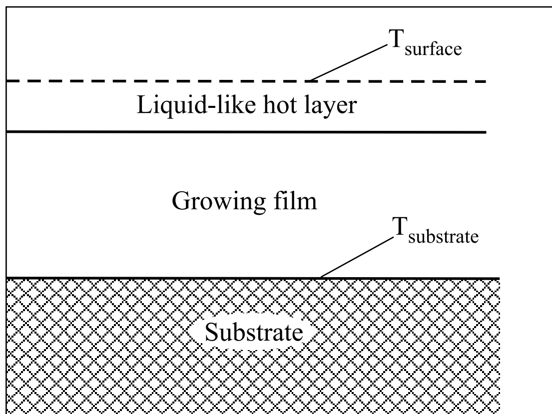

Fig.5. The formation of the growing film. The liquid-like hot layer exists until the atomic condensation takes place. This layer constantly moves keeping on the top of the growing film

Let us now estimate thermal conductivity of this layer based on the following model [9, 15]. We assume that during atomic condensation the thin "hot layer" consisting of mobile atoms, which deliver the flux q_{in} (Eq. (1)), is forming on the condensation surface. The high mobility of atoms allows considering the layer as a liquid-like. Obviously, the layer exists until the atomic condensation occurs. The layer constantly moves keeping on the top of growing solid film. Since atoms in the layer are bound to each other with metallic bonds, the layer contains both the ion and the electron subsystems. Main part of the energy in the layer is accumulated within the ion subsystem. Actually, atoms arriving on the condensation surface and forming the ion subsystem possess the kinetic energy E_a. The average velocity of ions within the layer is $v_i \sim v_a = \sqrt{2E_a/M_a}$ where M_a and v_a are the mass and the velocity of arriving atoms. The average velocity v_0 of electrons related to the kinetic energy E_a within the layer $v_0 \sim v_a$ because they belonged to the condensing atoms before they formed the electron subsystem. Since $m_e \ll M_a$ (m_e is the electron mass) it is clear that the average kinetic energy of electrons $E_0 \ll E_a$. Thus, the main part of the energy delivered by q_{in} and stored in the layer is accumulated by the ion subsystem but its transmission to the electron subsystem is strongly depressed because $M_a \gg m_e$ [16]. Note that the energy of the electron subsystem rapidly equilibrates with the energy E_e of the electrons of the solid film due to transport properties of electrons, while their velocity becomes v_e.

The thermal conductivity k_e of metals is mostly determined by electrons and reads

$$k_e = \lambda_e c_e v_e/3, \qquad (5)$$

where λ_e is the mean free path, c_e is the specific heat and v_e is the average velocity of electrons [17]. Because (i) the energy (i.e., heat) of the layer is accumulated in the ion subsystem and (ii) its transmission to the electrons is strongly limited, the effective thermal conductivity of the layer is defined by its ion subsystem. To estimate the effective thermal conductivity k_a we substitute all the parameters relating to the electrons by the corresponding parameters of the ions. That is, to obtain k_a, k_e given by Eq. (5) should be multiplied by the factor $m_e/M_a \times \times \lambda_a/\lambda_e \times v_a/v_e$, where m_e/M_a determines the decrease in the rate of energy transfer from ions to electrons, $\lambda_a/\lambda_e \times v_a/v_e$ characterizes the decrease in the thermal conductivity due to both the decrease of the mean free path λ_a and average velocity v_a of ions. Thus, we obtain $k_a/k_e \sim 10^{-10}$ that is, the effective thermal conductivity of the layer is strongly depressed. Comparing the thermal conductivity estimated, $k_a/k_e \sim 10^{-10}$, with that obtained from the experiment, $k_l/k_{bulk} \sim 10^{-9}$, we observe reasonable agreement between the experiment and our estimations. The discrepancy probably comes from the fact that the real thickness d_l of the layer is not known. On the other hand, the observed reasonable agreement, $k_a \sim k_l$, demonstrates that the described above mechanism accounts for the physics related to the transport of heat at the surface. For example, it is possible that the energy of the layer is dissipated by phonon-like mechanism. However for metals both liquid and solid it is very low [17]. Moreover, taking into account that d_l is much smaller than the average wave-length of

phonon, we conclude that the phonon mechanism is not efficient. The last mechanism of the energy dissipation is the emission of IR-radiation from the layer, just what we register measuring the surface temperature. The observed low thermal conductivity is conditioned by the very limited energy exchange between adatoms in the layer and solidified film beneath it. This "hot" layer represents a substance separating the vapor phase from the solid and can be viewed as a liquid-like layer.

In conclusion, the effect of the high temperature of the condensation surface developing during the condensation of the flux of sputtered atoms has been discovered for the first time by means of in situ temperature measurements. This temperature is determined by the flux of the energy delivering by condensing atoms, rapidly grows as the condensation has started, exists only during the deposition and steeply decays as the condensation is interrupted. The effect is explained by the extremely low thermal conductivity of the thin layer, which is formed by mobile atoms arriving on the condensation surface. This layer can be viewed as a new state of matter characterized by the extremely low thermal conductivity.

---

1. K. L. Chopra, *Thin Film Phenomena*, McGraw-Hill Book Comp. New York, 1969, p. 159.
2. M. V. Belous and C. M. Wayman, J. Appl. Phys. **38**, 5119 (1967).
3. G. Breitweiser, B. N. Varadarajan, and J. Wafer, J. Vac. Sci. Technol. **7**, 274 (1969).
4. E. Yoda, in *Proc. 6th Intern. Conf. Electron Microscopy*, Kyoto, 1966, p. 517.
5. D. D. Thornburg and C. M. Wayman, J. Appl. Phys. **42**, 4071 (1971).
6. M. Laugier, Thin Solid Films **67**, 163 (1980).
7. D. Daineka et al., Thin Solid Films **468**, 298 (2004).
8. M. Wakagi et al., J. Vac. Sci. Technol. A **13**, 1917 (1995).
9. L. R. Shaginyan, V. R. Shaginyan, and J. G. Han, Eur. Phys. J. B **46**, 335 (2005).
10. *Smithells Metals Reference Book*, 7th edn., Eds. E. A. Brandes, G. B. Brook, Elsevier, G.B., 1998.
11. M. Ohring, *The Materials Science of Thin Films*, 2nd ed. Academic Press, New York, 2002, p. 249.
12. J. F. Daviet, L. Peccoud, and F. Mondon, J. Appl. Phys. **73**, 1471 (1993).
13. L. Maissel, in: *Handbook of Thin Film Technology*, Eds. L. Maissel and R. Glang, McGraw-Hill Book Comp. New York, 1970, p. 309.
14. H. Kersten et al., Vacuum **63**, 385 (2001).
15. L. R. Shaginyan, J. G. Han, and N. V. Britun, Jap. J. Appl. Phys. A **44–45**, 3200 (2005).
16. E. M. Lifshitz and L. P. Pitaevskii, *Physical Kinetics*, Butterworth-Heinemann Ltd, Oxford, 2002.
17. D. Tabor, *Gases, Liquids and Solids*, 3rd ed., Cambridge University Press, Cambridge, 1991, p. 247.