

# Melting and dissociation of thin Au films into droplets on the inert Al<sub>2</sub>O<sub>3</sub> surface under thermal treatment

D. G. Gromov\*, S. A. Gavrilov, E. N. Redichev, and S. V. Dubkov

Department of Materials and Processes of Solid State Electronics, Moscow Institute of Electronic Technology (Technical University), 124498 Moscow, Zelenograd, Russia

## ABSTRACT

The process of thin polycrystalline Au films dissociation into droplets on the inert Al<sub>2</sub>O<sub>3</sub> surface during heating in vacuum was studied. It was shown that this process has no strictly determined temperature. Its melting temperature is essentially lower than that specified in reference books. Nevertheless it was shown that the dissociation process goes through the melting stage and its appearance is conditioned by the thin film surface, and on the whole its temperature reduces when the thin film thickness decreases. However, it was found that as Au film thickness decreases below 20 nm, the process activation energy starts to increase, and the dissociation process temperature also increases. This can be explained by the fact that at lower thicknesses a substrate substantially affects a film behavior.

**KEYWORDS:** gold, melting, phase transition, surface diffusion, thin film, agglomeration, dewetting

## INTRODUCTION

Recently with the development of nanotechnologies the researchers' attention has been focused on low-dimension systems. The characteristic feature of these systems is a number of dimensional effects which emerge inside of them. These effects lead to the change of physical, chemical and electric properties of materials [1] which are the basis of nanotechnology components.

Melting temperature decrease effect of low-sized objects is well known [1-23], including gold nanoparticles [24-28]. Classical equilibrium thermodynamics shows that if a system is restricted by a surface, whose energy is compared to the system bulk energy, as object  $r$  size decreases a monotone phase transition temperature decreases as  $T \sim f(1/r)$ .

At the same time, it is known that a heating of thin film often results in its disintegration (agglomeration or dewetting, in another words) into droplets [29-34]. More over, it was found [29], that there is no strictly determined temperature of this process for thin copper films, and it has an incubation period which reduces with heat temperature increase. Particularly, a thin copper film with a thickness of 20 nm started to disintegrate at a temperature of 610 °C after 5 min., and it also started to disintegrate at 470 °C but after 3h 40min. A film with a thickness of 100 nm started to disintegrate at 740 °C after 7 min., and at 640 °C after 2h 25min. It was shown that this process had an activation character.

It is the authors' [30-34] opinion that agglomeration occurs via a two-step mechanism consisting of (1) void nucleation by grain boundary grooving and (2) surface-diffusion-limited film dewetting and islanding.

It is the authors' [29] opinion that disintegration of thin film is a melting process.

In this paper we report a study of the kinetics of disintegration of initially continuous gold films into droplets on Al<sub>2</sub>O<sub>3</sub> surface. Our work covers

---

\*gromov@optolink.ru

the further study and analysis of such effects as melting temperature decrease and thin films dissociation into droplets in order to understand some of their peculiarities.

## METHODOLOGY

Pyroceram covered with a 0.5 micrometer thick layer of  $\text{Al}_2\text{O}_3$  was used as a substrate since it does not react chemically with gold. To form the samples rectangular substrates of  $3 \times 30$  mm were used. Thick-film electrodes were formed along the samples' edges that provided a reliable electric contact with the film under study. Thin Au films were formed on the substrate using vacuum evaporation method with a residual pressure of  $2 \cdot 10^{-6}$  Torr and at a room temperature of the substrate. Au layers thicknesses varied from 10 to 100 nm. The study of the films showed that Au films were always polycrystalline.

A special measurement complex was used to study the temperature and time dependence of dissociation process of a thin Au film into droplets [29]. This complex allows us measuring the current through the sample during its heating in vacuum with a residual gas pressure of  $1 \cdot 10^{-5}$  Torr. A resistive heating furnace was used to perform thermal treatment and the temperature inside the furnace was controlled with thermocouples. When the film breaks the sample, resistance starts to increase. As a result the current going through the sample decreases which leads to the voltage decrease on the auxiliary resistor that is registered by an electric recorder. Drastic drop of the current through the sample marks the beginning of the process of dissociation into droplets.

The samples surface morphology on different stages of the experiment was studied using scanning electron microscopy (SEM) and atomic force microscopy (AFM): initial sample and, annealed samples before and after the drastic decrease of the current through the sample.

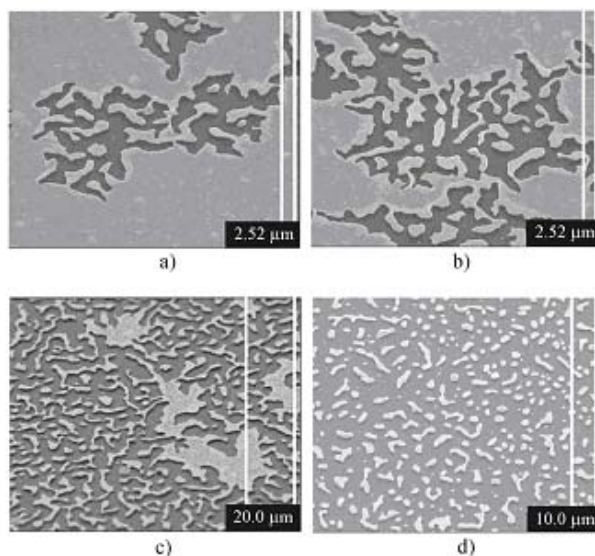
## RESULTS

The investigation of samples surface by AFM showed that the surface roughness after  $\text{Al}_2\text{O}_3$  deposition had the value  $\sim 2$  nm. The 10-nm-thick Au film was continuous, but grain boundary

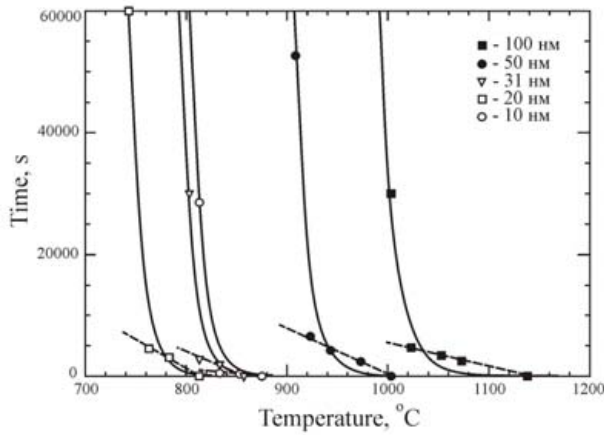
grooving was observed regardless the deposition on non-heated substrate was realized [35]. The grooving thickness corresponds to film thickness 10 nm. The grooving vanished with Au thickness increase. Au 50-nm-thick film had the roughness  $\sim 4$  nm and film grain size about 25-30 nm.

It was found, that there was no strictly determined temperature of dissociation into droplets for Au films. For example, 100 nm Au film started to dissociate at 1130 K after 30 sec., and it also started to dissociate at 1020 K but after about  $\sim 4700$  sec. A 20 nm thick film started to dissociate at a temperature of 810 K after 30 sec., while it also dissociated at a temperature of 760 K but after  $\sim 4500$  sec. Similarly to copper, thin Au film dissociates locally at any place of the sample and then spreads front edge (Fig. 1). As a result it is possible to distinguish 3 sample regions: the region where the film remains continuous (Fig. 1 (a)); the region where the film is totally dissociated into droplets (Fig. 1 (b)), and regions where there are film breaks with droplets inside of them (Fig. 1(c)).

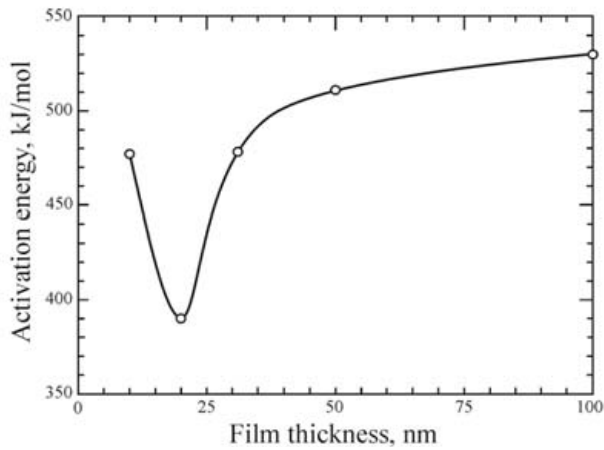
Fig. 2 shows the time dependences before the beginning of dissociation into droplets on the



**Fig. 1.** SEM images of the gold thin film at different stages of melting-disintegration: (a) the appearance of a rupture on a continuous film, (b, c) gradual expansion of the melting-disintegration area, and (d) the complete film disintegration into droplets.



**Fig. 2.** The time of the onset of melting-disintegration for gold thin films of different thicknesses as the function of the annealing temperature under vacuum.



**Fig. 3.** Experimental dependence of the activation energy for the melting-dispersion process on the film thickness for the gold thin film.

annealing temperature for Au film of different thickness. Taking into account similar behavior of gold and copper films we approximated experimental points to the following function:

$$t = \frac{A}{\exp\left(\frac{E_a}{RT}\right)}, \quad (1)$$

which follows the known Arrhenius equation. Although correlation coefficients turned out to be close to 1 (0.82–0.96 for different thicknesses) it can be seen by eye that the experimental points do

not coincide with approximation curves well enough. The fact which attracts our attention is that Au films with all thicknesses have some experimental points which coincide with a direct line (Fig. 2). It should be noted however that this was not observed on copper films [29].

Nevertheless, the experimental data approximation allowed us to estimate a variation in the energy of activation of the process of dissociation into droplets with variation of Au film thickness. According to calculations when gold films thickness increases from 20 to 100 nm,  $E_a$  value increases from 390 to 530 kJ/mole (Fig. 3).

An unexpected fact is that 10 nm thick Au films require higher temperatures to be dissociated totally than 20 nm thick films (Fig. 2). As a result the activation energy dependence on thickness has an extreme character in contrast to copper films [29], which can be seen in Fig. 3.

## DISCUSSION

Authors [30–34] explain thin film disintegration into droplets from the position of surface diffusion. However, this is not quite correct. By definition a diffusion is a mass transfer in consequence of thermal motion of substance particles in direction of their concentration decrease. A volume diffusion leads to their uniform distribution throughout volume. A surface diffusion results in uniform distribution of particles throughout surface. In the considered case we handle with absolutely contrary effect: a process proceeds from uniform surface distribution of particles to collection into droplets, i.e. in the direction to concentration increase.

Moreover, in accordance with the phenomenological model [32] the presence of grooving of initial 10-nm-thick Au film should be encourage to additional reduction of film disintegration temperature, but we observe that it is higher in comparison to 20-nm-thick Au film.

In our opinion film disintegration into droplets has two aspects: thermodynamic and kinetic.

The surface is the main defect of a three-dimensional crystal lattice and its vibration spectrum differs from the solid one. An established fact is that vibration amplitude of atoms in the crystal lattice, placed near the surface is 40–100% higher than that of solid ones [35–37]. As a result,

Debye temperature of near-surface layers is 30-50% lower than that of a solid material [36, 37]. In accordance with the Lindemann criterion and a number of experimental observations, the melting process starts from the surface and moves inside and to the centre.

Based on the equilibrium of liquid and solid phases in the melting point, considering a surface contribution and with the assumption of invariable transition from ordered crystalline state to disordered liquid state ( $\Delta S(T)=\text{const}$ ), a known equation comes to light which describes a decrease of thin film melting temperature depending on its thickness  $h$  [2].

$$T \approx T_{\infty} \left( 1 + \frac{\Delta\sigma}{\Delta H} \frac{2}{h} \right), \quad (2)$$

where  $\Delta\sigma$  - surface energy variation as a result of transition from crystalline to liquid state;  $T_{\infty}$  - material melting temperature specified in reference books;  $\Delta H$  - enthalpy variation during transition from crystalline to liquid state.  $\Delta S$  - entropy variation during transition from crystalline to liquid state.

Assuming that a surface layer, exposed to melting is initially a thin film of material lying on the surface of this material, one can get the following formula from the equation (2)

$$h = \frac{T_{\infty} \Delta\sigma}{(T - T_{\infty}) \Delta H(T_{\infty})}. \quad (3)$$

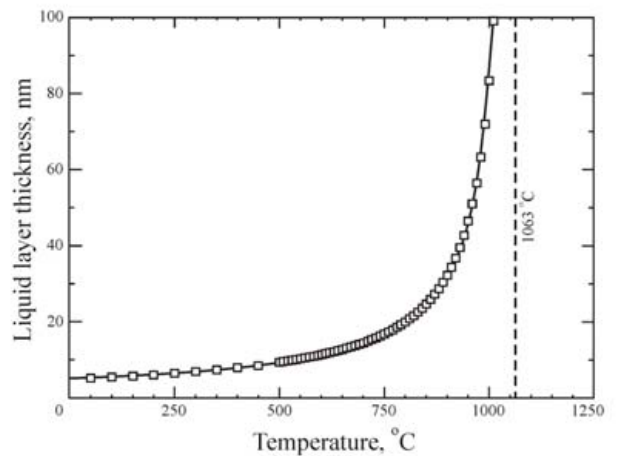
Expression (3) allows us to calculate the dependence between the thickness of the molten layer and the Au temperature, using the following initial data. For a free top Au film surface the following values of Au surface energy were taken  $\sigma_{TB}=1,45 \text{ J/m}^2$  and  $\sigma_{JK}=1,125 \text{ J/m}^2$ , which border on vacuum [38]. For a solid phase boundary “gold-to-gold” the  $\sigma_{TB}=1,45 \text{ J/m}^2$  value was used, and for the boundary “liquid gold-to-solid gold” the value  $\sigma_{JK}=1,29 \text{ J/m}^2$  was taken. Melting heat for Au unit of volume is  $\Delta H(T_{\infty})=1,24 \times 10^9 \text{ J/m}^3$  [39].

Fig. 4 shows a calculated dependence of the molten surface layer thickness on Au temperature. Fig. 4 demonstrates that melting of a semi-infinite system has heterogeneous nature with the following features:

- The system becomes totally molten at an equilibrium melting temperature of a solid material specified in reference books;
- At a temperature lower than that specified in reference books, there exists a liquid layer with a certain thickness on the solid phase surface which is brought to equilibrium with the solid phase. The lower the temperature the thinner the liquid phase layer on the surface is.

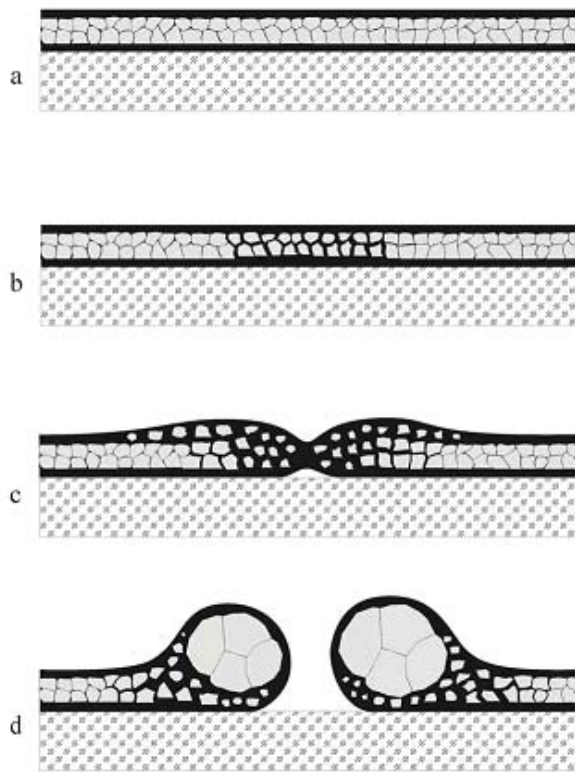
This melting character of a semi-infinite system allows us to assume the following mechanism of a thin Au film dissociation, which explains the reason why there is no certain dissociation temperature.

In accordance with the results obtained with AFM it is evident that a thin Au film of, for example 50 nm, consists of crystal grains arranged in not more than two layers. According to heterogeneous melting features during heating, an original liquid phase is generated on top and bottom surfaces of the thin film, that wets and partially dissolves (not necessarily completely dissolves) the thin film crystal grains along the boundaries. Liquid layer thickness depends on temperature. As Fig. 2 shows, 50 nm Au film dissociation into droplets was observed at a temperature interval of 903-1003 K. A calculation curve in Fig. 4 shows that both at 903 K and at 1003 K there should exist a liquid layer on top and bottom of thin Au film



**Fig. 4.** The heterogeneous melting of gold: the calculated dependence of the surface melting layer thickness on the temperature.





**Fig. 5.** Schematic diagram illustrating the melting–dissociation process in the gold thin film on an inert surface: (a) liquid layer appearance on the surfaces of the thin polycrystal film; (b) liquid penetration into the whole bulk of the film in the local area and partial dissolving of grains; (c) liquid phase flowing into native solid phase to entrain the crystallites drifting in it and to cause a thin film rupture; (d) droplet formation with subsequent crystallization accompanied by a release of heat responsible for further melting of the film.

surfaces of nearly the same thickness: for example 12 and 16 nm respectively. This stage is schematically displayed in Fig. 5(a).

Well wetting and grain boundaries during heating lead to the penetration of the liquid phase into the entire thickness of the film (Fig. 5(b)). Liquid distribution caused by wetting determines a kinetic constituent of the process of thin film dissociation into droplets: at higher temperatures the liquid viscosity is lower and dispersion process starts quickly; at lower temperatures the viscosity is higher, wetting goes on slower and dispersion starts after some time and goes on slower.

Because of liquid phase fluidity, good wetting of its own crystalline solid phase, bad wetting of the

inert substrate surface, the surface tension force reduces the thin film surface area, using an excessive thin film surface energy. As a result, liquid phase leaks on its own solid phase, carrying along crystal grains and thus causing void nucleation (Fig. 5(c)). Surface energy reduction shifts the equilibrium between liquid and solid phase to the area of higher temperatures, which makes existence of such number of liquid phase at a given temperature impossible. That's why at the same temperature the process of liquid crystallization starts easier (as the expenditure of energy is not required to create interface). Liquid crystallization is accompanied by local heat release, which causes a melting effect of the solid polycrystalline film (Fig. 5(d)) and therefore, the emergence of a moving front where the process of melting–dissociation takes place.

Thus, the thermodynamic aspect consists in that a melting temperature of thin film decreases with film thickness reduction. It can be predicted from thermodynamic data [23]. At the same time void nucleation and dewetting are related to the kinetic aspect. The process of dissociation of thin film into droplets is not directly melting. Nevertheless the melting caused by the surface or, in other words, heterogeneous melting of a semi-infinite system is the main component of the process. The heterogeneous melting phenomenon and its manifestations in a number of another processes have been considered in detail in [40].

We have no definite explanation to the existence of linear section on the curves in Fig. 2 and the absence of such for copper. As it follows from our discussion, film dissociation into droplets is a multistage process. The slowest stage determines the entire speed of the process. The emergence of a linear section on dependences depends on the fact, that during thin Au films dissociation, one of the stages has a respective dependence and is the slowest for the given temperature range. The comparison of gold and copper properties shows the proximity of these materials in basic characteristics, affecting the process of thin film dissociation, such as melting temperature and the surface energy of liquid and solid phases. But gold and copper differ substantially in viscosity value. Gold viscosity (5,0 MPa·s) is 1.5 times higher than that of copper (3,3 MPa·s). That's why we can assume that a higher Au viscosity

conditions the slowdown of dissociation process of the thin film into droplets and the emergence of a near-linear curve section in Fig. 2.

Activation energy growth depending on the increase of Au film thickness is natural since the surface energy value which falls on the volume unit decreases, and the amount of the material which should be exposed to mass transfer from the film into droplets increases. The extreme character of the dependence of activation energy of the dissociation process into droplets on the thickness of Au film can be explained by the increasing influence of underlying  $\text{Al}_2\text{O}_3$  layer when the film thickness reduces below 20 nm [41]. In the extreme case, when a thin film thickness is several mono-layers, it virtually becomes an adsorbed layer, lowering the substrate surface energy. In this case, thin film material atoms tend to distribute evenly on the substrate surface area and dissociation into droplets is impossible. It is clear that an Au film thickness of 10 nm is intermediate when the substrate influence is tangible, i.e. spread to the noticeable depth in the Au film and causes an evident difficulty during the process of dissociation into droplets.

## SUMMARY

It was found that the dissociation process of thin Au film into droplets can go on, depending on the temperature, at a different speed, which is conditioned by kinetic reasons. The dissociation of thin Au film of the same thickness can occur at a different time and at different temperatures, being instant at higher temperatures and taking several hours at lower ones. This means that the process has an activation character. The dissociation starts locally and then spreads front edge.

The main reasons which cause this process are heterogeneous melting, causing the liquid layer emergence on the surface, and the system tending to lower its energy at the expense of lowering absolute surface energy. This can be achieved by the decrease of specific surface energy as a result of transition from solid to liquid state, and a system surface area reduction, which is possible in liquid state, when the system is fluid, and the surface tension force is capable of doing work.

As film thickness decreases, the moment comes when the film dissociation into droplets becomes difficult. This happens when a thin film stops

being an independent system, having its unique properties, and becomes the part of the other system, i.e. the substrate on which surface the film was deposited.

## REFERENCES

1. Andrievski, R. A. 2009, *Rev. Adv. Mater. Sci.*, 21, 107.
2. F. Komnik, Yu. 1979, *Physics of Metallic Films: Size and Structural Effects*, Atomizdat, Moscow (in Russian).
3. Geguzin, Ya. E. 1984, *Physics of Sintering*, Nauka, Moscow (in Russian).
4. Gusev, A. I. and Rempel, A. A. 2004, *Nanocrystalline Materials*, Cambridge International Science, Cambridge.
5. Tartaglino, U., Zykova-Timan, T., Ercolessi, F., and Tosatti, E. 2005, *Phys. Rep.*, 411, 291.
6. Müller, P. and Kern, R. 2003, *Sur. Sci.*, 529, 59.
7. Pluis, B., Denier van der Gon, A. W., and van der Veen, J. F. 1990, *Sur. Sci.*, 239, 265.
8. Kofman, R., Cheyssac, P., Lereah, Y., and Stella, A. 1999, *Eur. Phys. J. D*, 9, 441.
9. Manai, G. and Delogu, F. 2007, *Physica B*, 392, 288.
10. Safaei, A., Attarian Shandiz, M., Sanjabi, S., and Barber, Z. H. 2007, *J. Phys.: Condens. Matter.*, 19, 216216 (9pp).
11. Zayed, M. K., Hegazy, M. S., and Elsayed-Ali, H. E. 2004, *Thin Solid Films*, 449, 254.
12. Tartaglino, U. and Tosatti E. 2003, *Sur. Sci.*, 532-535, 623.
13. Bottani, C. E., Li Bassi, A., Tanner, B. K., Stella, A., Tognini, P., Cheyssac, P., and Kofman, R. 2001, *Mater. Sci. Eng. C.*, 15, 41.
14. Lu, K. and Jin Z.H. 2001, *Curr. Opin. Solid State Mater. Sci.*, 5, 39.
15. Friso van der Veen, J. 1999, *Sur. Sci.*, 433-435, 1.
16. Wojtczak, L. and Rutkowski, J. H. 1998, *Progr. Surf. Sci.*, 59, 79.
17. Ross, J. and Andres R. P. 1981, *Sur. Sci.*, 106, 11.
18. Sakai, H. 1996, *Sur. Sci.*, 351, 285.
19. Celestini, F. and Ten Bosch, A. 1995, *Phys. Lett. A*, 207, 307.
20. Peters, K. F., Chung, Y.-W., and Cohen, J. B. 1997, *Appl. Phys. Lett.*, 71, 2391.
21. Manai, G. and Delogu, F. 2007, *J. Mater. Sci.*, 42, 6672.

- 
22. Gromov, D. G., Gavrilov, S. A., and Redichev, E. N. 2005, *Rus. J. Phys. Chem.*, 79, 1578.
  23. Gromov, D. G., Gavrilov, S. A., Redichev, E. N., Klimovitskaya, A. V., and Ammosov, R. M. 2006, *Rus. J. Phys. Chem.*, 80, 1650.
  24. Sambles, J. R. 1971, *Proc. R. Soc. Lond. A*, 324, 339.
  25. Buffat, P. and Borel, J. P. 1976, *Phys. Rev. A*, 13, 2287.
  26. Ercolessi, F., Andreoni, W., and Tosatti, E. 1991, *Phys. Rev. Lett.*, 66, 911.
  27. Plech, A., Cerna, R., Kotaidis, V., Hudert, F., Bartels, A., and Dekorsy, T. 2007, *Nano Lett.*, 7, 1026.
  28. Wang, N., Rokhlin, S. I., and Farson, D. F. 2008, *Nanotechnology*, 19, 415701 (7pp).
  29. Gromov, D. G., Gavrilov, S. A., Redichev, E. N., and Ammosov, R. M. 2007, *Phys. Solid State*, 49, 178.
  30. Jiran, E. and Thompson, C. V. 1990, *J. Electron. Mater.*, 19, 1153.
  31. Jiran, E. and Thompson, C. V. 1992, *Thin Solid Films*, 208, 23.
  32. Saxena, R., Frederick, M. J., Ramanath, G., Gill, W. N., and Plawsky, J. L. 2005, *Phys. Rev. B*, 72, 115425.
  33. Danielson, D. T., Sparacin, D. K., Michel, J., and Kimerling, L. C. 2006, *J. Appl. Phys.*, 100, 083507.
  34. Beszeda, I., Szabo, I. A., and Gontier-Moya, E. G. 2004, *Appl. Phys. A*, 78, 1079.
  35. Shigeta, Y. and Fukaya, Y. 2004, *Appl. Sur. Sci.*, 237, 21.
  36. Goodman, R. M., Farrell, H. H., and Somorjai, G. A. 1968, *J. Chem. Phys.*, 48, 1046.
  37. Kiselev, V. F., Kozlov, S. N., and Zoteev, A. V. 1999, *Fundamentals of Physics of Solid Surface*, Izd. Moskovskogo Univ., Moscow, [in Russian].
  38. Babichev, A. P., Babushkina, N. A., Bratkovskii, A. M., *et al.* 1991, *Physical Values: A Handbook*, Grigor'ev, I. S. and Meilikhov, E. Z. (Eds.), Energoatomizdat, Moscow, (in Russian).
  39. Emsley, J. 1989, *The Elements*, Clarendon, Oxford.
  40. Gromov, D. G. and Gavrilov, S. A. 2009, *Phys. Solid State*, 51, 2135.
  41. Gromov, D. G., Gavrilov, S. A., Redichev, E. N., Chulkov, I. S., Anisimov, M. Y., Dubkov, S. V., and Chulkov, S. I. 2010, *Appl. Phys. A*, 99, 67.