

The DSMC modeling with taking into account condensation process were carried out for the domain limited by the nozzle exit and distance $15 R$ from it in the X direction. The height of the computation domain was $10 R$. Boundary parameters at the plane of nozzle exit corresponds to parameters obtained within the computation in whole domain without taking into account the cluster formation process.

The simulation data show that there are no clusters in the jet for considered parameters of silver film deposition ($Q_{He}=36$ sccm and $T_0 < 1400$ K). Such conclusion is in agreement with estimations of [13]. In [13] for description of cluster formation process the parameter $\Gamma^* = \Gamma / \Gamma_{ch}$ was employed, where $\Gamma = n_0 d^{0.85} T_0^{-1.29}$, $d = 2R$, n_0 — the gas density inside crucible (Γ_{ch} depends on vapor properties). For considering cases $\Gamma^* < 200$ and according [12, 13] there is no cluster formation process within the jet.

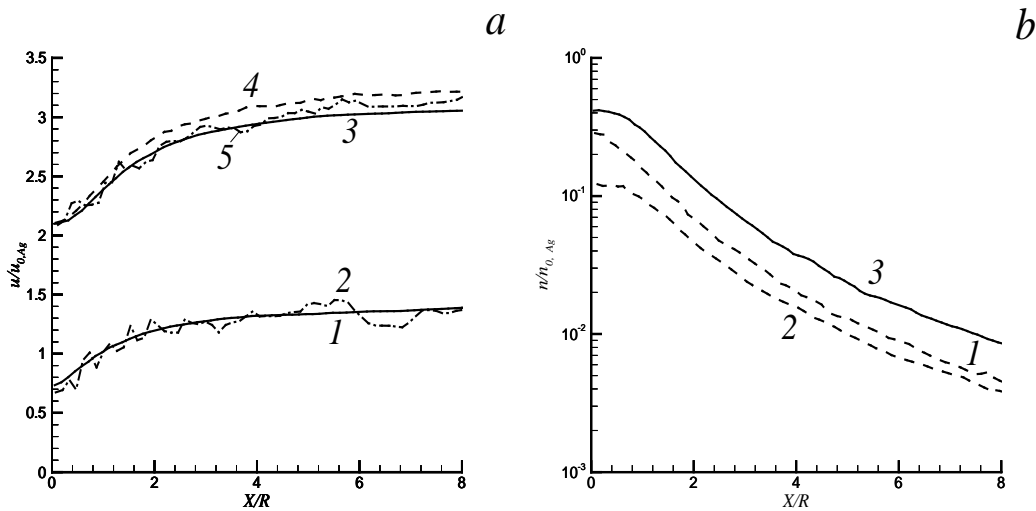


Fig. 9. (a) The velocity of particles in the silver jet (1 – Ag, 2 – Ag₂) and in the Ag-He jet (3 – Ag, 4 – He, 5 – Ag₂). (b) The dimensionless density of silver atoms in the pure silver jet (1), silver atoms in the Ag-He jet (2), helium atoms in the Ag-He jet (3). $T_0 = 2123$ K.

To define the parameters which correspond to the cluster appearance in the jet additional simulations were carried out (i) $T_0=1770$ K, $Q_{He}=0$, (ii) $T_0=1770$ K, $Q_{He}=1000$ sccm, (iii) $T_0=2123$ K, $Q_{He}=0$, (iv) $T_0=2123$ K, $Q_{He}=5000$ sccm.

The mole fractions of clusters in flowfield occur very small and less than 10^{-5} for the cases (i) and (ii). The main component of clusters is a dimer. The flow was rarefied for these cases, Knudsen numbers determined by parameters of gases in the crucible exit are in the order of 0.1. For higher value of the evaporation temperature $T_0=2123$ K mole fractions of clusters in the jet are approximately 10^{-3} (Fig. 8). Mole fractions of clusters are freezing at distance 1-2 R from the nozzle exit which is in agreement with the data of [31]. The maximal observed within simulation cluster size is 4 atoms. The helium load of $Q_{He}=5000$ sccm leads to acceleration of Ag atoms and clusters (Fig. 9a). The velocities of observed clusters are coincides approximately with the velocity of silver atoms. For such small flow clusterization degree there is no impact of condensation process on monomers parameters. The curves 1,3,4 in Fig. 9a and curves 1-3 in Fig. 9b coincide for the cases with and without taking into account cluster formation reactions.

5. Nanostructured silver film growth

Based on the set of experimental and calculated data, we can conclude that within considering experimental range of deposition parameters ($T_0 < 1400$ K, $Q_{He}=36$ sccm) the formation of

nanostructured film on the substrate surface occurs due to deposition of silver atoms only. The clusters in the jet is practically absent. The growth of the nanostructured film in this case occurs according to the Volmer-Weber mechanism [32]. The deposited atoms diffuse over the surface and nanoparticle nuclei are formed under collisions of such adatoms. The nonmonotonic dependence of the surface particle concentration (Fig. 2) proves this mechanism of nanostructure growth. After the stage of the surface nucleus formation process the next stage of particle size increasing begins. Then particle coagulation, the formation of “islands” of irregular form and transition to the percolation structure of the film are observed. The further rise of depositing mass leads to the formation of solid metal coating.

6. Conclusions

Nanostructured silver films were obtained by the gas-jet technique for the range of crucible temperatures $T = 1200\text{-}1400\text{ K}$. The direct simulation Monte Carlo method was applied for modeling the flow of a mixture of the silver vapor with a helium carrier gas inside the crucible with subsequent expansion of the mixture into vacuum as a free jet. The analysis of simulation and experimental data showed the following:

1) The increase of the helium flux for a fixed crucible temperature leads to non-monotonic behavior of the silver atom nozzle flux. Firstly the silver flux rises, reaches a maximal value and then slowly decreases. The helium gas accelerates the silver atoms that results in significant rise of the mass flow rate of silver vapor. As a result, the presence of the carrier gas promotes the rise of the silver flux to a remote substrate which is a positive factor for film deposition by the gas-jet method. The silver flux distribution along the substrate surface is found to be fairly uniform that is also an advantage of the considered deposition technique.

2) The presence of a background gas in the vacuum chamber leads to decrease of the silver atom flux onto the substrate and thus reduces the deposition efficiency. A simple scattering model can be used for estimation of the effect of background gas in the deposition process.

3) There are no clusters formed in the jet for the considered conditions (the crucible temperature is below 1400K and helium load is less or equal 36 sccm). The cluster formation process starts in the jet at sufficiently higher crucible temperatures and helium fluxes.

4) The flow estimations based on the inviscid continuum model are very rough and does not match the considered flow regimes. Estimations of silver vapor flow parameters for low temperatures of the crucible without carrier gas load may be done on the base of free-molecular relations. In general, DSMC (or other methods based on solving the Boltzmann equation) should be employed for adequate prediction of flow parameters.

5) The formation of the observed nanostructured silver films by the gas-jet deposition method for the considered parameter range is a result of nanocluster formation directly at the substrate surface due to diffusion and nucleation of the deposited silver atoms.

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References

- [1] S. Jalili, E.M. Goliaei, J. Schofield // *Int. J. of Hydrogen Energy* **42(21)** (2017) 14522.
- [2] M. Haruta // *Chem. Rec.* **3** (2003) 75.

- [3] N.R. Agarwal, F. Neri, S. Trusso, A. Lucotti, P.M. Ossi // *Appl. Surf. Sci.* **258** (2012) 9148.
- [4] S.H. Cho // *Phys. Med. Biol.* **50** (2005) 163.
- [5] I. Yamada, T. Takagi // *IEEE Trans. Electron Devices* **ED-34(5)** (1987) 1018.
- [6] P. Gatz, O.F. Hagen // *Appl. Surf. Sci.* **91** (1995) 169.
- [7] K. Wagner, P. Piseri, H.V. Tafreshi, P. Milani // *J. Phys. D: Appl. Phys.* **22** (2006) R439.
- [8] M.N. Andreev, A.K. Rebrov, A.I. Safonov, N.I. Timoshenko // *Nanotechnologies in Russia* **6(9–10)** (2011) 587.
- [9] M.J. Aziz // *Appl. Phys A* **93** (2008) 579.
- [10] C. Polop, C. Rosiepen, S. Bleikamp, R. Drese, J. Mayer, A. Dimyati, T. Michely // *New J. Phys.* **9** (2007) 1.
- [11] S.V. Starinskiy, V.S. Sulyaeva, Yu.G. Shukhov, A.G. Cherkov, N.I. Timoshenko, A.V. Bulgakov, A.I. Safonov // *J. Struct. Chem.* **58(8)** (2017) 1581.
- [12] O.F. Hagen // *Surf. Sci.* **106** (1981) 101.
- [13] O.F. Hagen // *Z. Phys. D* **20** (1991) 425.
- [14] H. Ashkenas, F.S. Sherman, In: *Rarefied Gas Dynamics*, ed. by J.H. de Leeuw (N.Y.: Academic Press, 1965), p.84.
- [15] G.A. Bird, *Molecular gas dynamics and the direct simulation of gas flows* (Clarenton Press: Oxford, 1994).
- [16] G.A. Bird // *Phys.Fluids* **23** (2011) 106101.
- [17] I.B. Sebastio, A. Alexeenko // *Physics of Fluids* **28** (2016) 107103.
- [18] S. Gimelshein, I. Wysong // *Physics of Fluids* **29** (2017) 067106.
- [19] N.Y. Bykov, Yu.E. Gorbachev // *Appl. Math. Comp.* **296** (2017) 215.
- [20] <https://www.powerstream.com/vapor-pressure.htm>
- [21] https://www.webelements.com/silver/atom_sizes.html
- [22] Yu.A. Koshmarov, Yu.A. Ryzhov, *Applied Dynamics of Rarefied Gas* (Mashinostroenie, Moscow, 1977). (In Russian)
- [23] A.K. Rebrov, In: *Rarefied Gas Dynamics*, ed. by O.M. Belotserkovskii (N.Y.: Springer, 1985), p.849.
- [24] A.V. Bulgakov // *SPIE Proc.* **2403** (1995) 75.
- [25] A.V. Bulgakov, M.R. Predtechensky, A.P. Mayorov // *Appl. Surf. Sci.* **96-98** (1996) 159.
- [26] B.M. Smirnov // *Phys. Usp.* **40(11)** (1997) 1117.
- [27] *Physico-chemical processes in gas dynamics. Electronic handbook in 3 volumes. Volume I: Dynamics of physico-chemical processes in gas and plasma*, ed. by G.G. Chernyi and S.A. Losev (Moscow: publishing house of Moscow University, 1995). (In Russian)
- [28] D.I. Zhukhovitskii // *J. Chem. Phys.* **101** (1994) 5076.
- [29] B.M. Smirnov, A.S. Yatsenko // *Phys. Usp.* **39** (1996) 211.
- [30] V.N. Kondratiev, E.E. Nikitin, *Kinetics and mechanism of gas-phase reactions* (Moscow: Nauka, 1974). (In Russian)
- [31] N.Y. Bykov, Yu.E. Gorbachev, V.V. Zakharov // *AIP Conf. Proc.* **1786** (2016) 050001.
- [32] J.A. Venables, G.D.T. Spliller, M. Hanbukah // *Rep. Prog. Phys.* **47(4)** (1984) 399.