Temperature and Entropy of Atomic Collisions Cascade at Interaction of Accelerated Ions with a Surface

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Abstract – The opportunity of description of atomic collisions cascades and atomic excitations in cascades in terms of base concepts of a nonequilibrium statistical physics is shown. The temperature and entropy of atomic collisions cascade in near-surface layer of solids at action by accelerated ions with energy about 10 keV are calculated. The pattern of atomic excitations in collisions cascades is offered. Empirical formulas for probability of ionization of secondary atoms most the useful in the practical relation are theoretically justified.

1. Introduction

The purpose of the present article – the description of sputtering of a solid surface by accelerated to keV energies ions and the phenomena at sputtering on the basis of principles of a non-equilibrium statistical physics. This operation is continuation of development of the thermodynamic approach to the description of processes at the sputtering which beginning in 1960th years by authors [1]. The theme urgency is caused by necessity of development of theoretical patterns for the phenomena and processes at interacting of the accelerated ions with a surface.

Now as a rule at calculations of probabilities of excitation and ionization of the secondary atoms the models grounded on consideration of processes in system «secondary atom-surface» is used as on their bottom it is possible to explain many experimental facts. Thus it is supposed, that excitations of atoms in atomic collisions cascades generally absence or do not give any contribution into states of secondary particles. However at such approach there is not up to the extremity clear a problem: where the internal energy of atoms which they gain at inelastic collisions in a cascade?

2. Temperature and entropy of atomic collisions cascade, the sputtering and excitation of the secondary atoms

Observe in particular a question on excitation of the secondary atoms. Being grounded on experimental data (in particular [2]) for the relative density of levels population for the secondary atoms we will obtain [3–6]

$$f_n = f_0 \exp\left(-\frac{E_n}{kT_e} + \frac{D_0}{kT_a}\right), \qquad (1)$$

were E_n is the energy of n level; D_0 is the atomization energy of surface layer; T_a and T_e are the atomization's temperature of sputtered material and excitation's temperature of registrant atoms; f_0 is the normalizing factor which is included the statistical sum on atoms states; k is the Boltzmann's constant.

Compare (1) with a non-equilibrium distribution function of molecules on the energy states, widely used for the description of density population vibrational levels of molecules in the molecular kinetics, in particular, in non-equilibrium molecular gas [3]:

$$f_n' = f_0' \exp\left(-\frac{nE_1}{kT_k} + \frac{nE_1 - E_n}{kT_t}\right). \qquad (2)$$

Distribution (2) presumed to consideration of plurality of energy levels of molecules as an independent subsystem with the temperature T_k which is in the thermostat, in the capacity of which gas of molecules as whole with the temperature T_t. Parameters E_1, E_n are energies of, accordingly, 1st and nst levels of the oscillator simulated a molecule; n is the number of the quantums occupying nst level. Relation (2) is known as Treanor's distribution [3].

Comparison (1) with (2) reveals concurrence of distribution functions under the shape, but, obviously, not on sense of parameters including temperature.

Distributions with 2 temperature parameters in a nonequilibrium statistical physics have been received on the basis of solutions of rate equation for a distribution function in nonequilibrium conditions. Later it was detected, that they can be received also from canonical distributions of Gibbs. Both techniques are enough general that these function (2) could be used for exposition of any statistical systems and not just gases.

View plurality of atomic collisions cascades on major number of initial ions, as a statistical ensemble. Then a separate cascade (caused by one initial ion) is statistical system. In the capacity of quasi-particles we shall view quantums of atoms excitation in cascades which arise at inelastic collisions of atoms and existing during time ($\sim 10^{-15} - 10^{-14}$ S) due to an opportunity of go-ahead transfer of excitations from atom to atom at collisions. Thus, an atomic collisions cascade – calorstat with the temperature T_a, quantums of excitations – a subsystem of quasi-particles with the temperature T_e. At such approach T_e in (1) and T_k in (2) it is necessary to give a sense of temperature of quasi-par-

ticles (quantums of excitations) and to the parameters T_a in (1) and T_t in (2) sense of cascade temperature.

On the basis of coincidence of the shape (1) and (2) and reference theoretical calculations for a case of atomic excitation in atomic collisions cascades in [4–6] the modified Treanor's distribution has been received:

$$f_n' = f_0' \exp\left(-\frac{nE_1}{kT_{ex}} + \frac{nE_1 - E_n}{kT_{cas}} \right) =$$

$$= f_0' \exp\left[E_1 \left(-\frac{n}{kT_{ex}} + \frac{n-1}{kT_{cas}} \right) - \frac{\Delta E}{kT_{cas}} \right], \qquad (3)$$

where $\Delta E = E_1 - E_n$ is the excitation energy at transition from a level E_1 on level E_n; T_{cas} is the temperature of an atomic collisions cascade; T_{ex} is the temperature of excitations (quasi-particles) in a stage. Note that (3) is transmuted into the Saha's formula at $T_{\text{cas}} = T_{ex}$ (the equilibrium).

Clearly, that in the atom moved in a solid the system of energy levels of electrons differs from the system of levels in free atom. So, in case of metals the polarization field of mobile electrons causes the shift in electronic density of exterior shells of atom in relation to a nucleus in a direction of moving, that gives in absence of the reference for a free atom of a set of quantum numbers [7]. Therefore, the analysis of correspondence (3) to experiment cannot be now detailed, taking into account transitions between concrete energy levels in atom. At the same time, as shown below, common analysis of correspondence (3) to many experimental facts is possible.

For calculations we shall consider volume of target V in which energy of an initial ion is absorbed, we shall term its "volume of cascade". Let it will be cylindrical volume with linear dimensions d about run of initial ion R (Fig. 1).

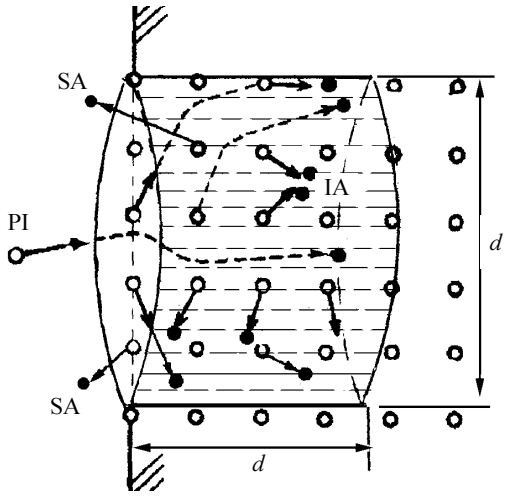

Fig. 1. The scheme of volume V of a atomic collisions cascade: PI – primary ion; SA – sputtered atoms, IA – implanted atoms which have been knocked off from equilibrium point lattice as a result of development of a cascade; d – linear dimensions of cascade

The given volume in time development of a cascade ($\tau_c \sim 10^{-15} - 10^{-14}$ s) can be considered as isolated because the time of cascade development τ_c is less than time of a thermalization τ_t of the absorbed energy ($\tau_t \sim 10^{-10} - 10^{-11}$ s). At energy of initial ion $E_0 \sim 10$ keV its run in metals $R \sim 100$ Å. The number of atoms in volume of cascade V is equal to $N = Vc = \pi d^3 c \approx 40000$ (c is the characteristic atom density in solids, for metals $c \sim 10^{22}$ atoms/cm^3). Number n' of atoms of the solid in V displaced from equilibrium standings as a result of development of cascade which created by initial ions with $E_0 \approx 10$ keV: $n' \approx E_0/2E_{dis} \approx 200$ (on the basis of experiment and the theory of passage of charged particles through substance [9]); $E_{dis} \approx 25$ eV is energy of a atom displacement from point of the lattice. The temperature of a cascade can be determined in nonequilibrium sense as $T_{cas} = dU/dS$, where dU is the increasing of an internal energy of volume V due to development of a cascade. According to [8], $dU = E_{dis}n' \approx 5000$ eV. The increasing of an entropy dS according to Boltzmann's formula is defined as $dS = k\ln[N!/(N - n')!n'!]$ [8] or with use for factorials of a Stirling's formula, as

$$dS = k[N\ln N - (N - n')\ln(N - n') - n'\ln n'] \approx 0.1 \text{ eV/K};$$

$$T_{cas} = dU/dS \approx 50000 \text{ K} \approx 4.3 \text{ eV}.$$

The given quantity well corresponds to the most probable energy in energy distributions of secondary atoms known from experiment, that is the strong corroborating of objectivity of conceptions developed here. In Figs. 2 and 3 are shown the dependences of cascade entropy and temperatures from number displaced atoms in volume V (in these and subsequent figures the curves are simulated with the help of programming in Microsoft Excel of formulas (3) and which given in the text).

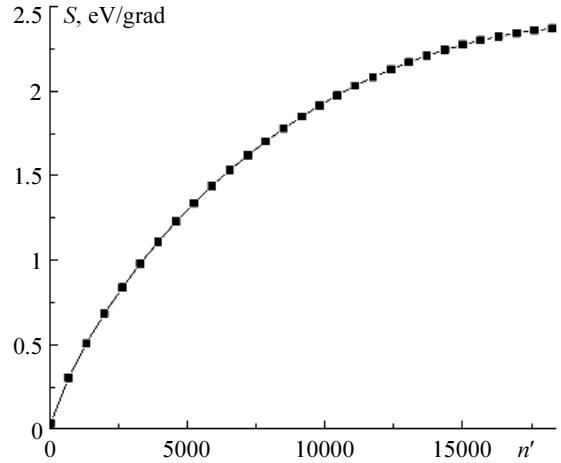

Fig. 2. Entropy of volume of cascade in dependence on number of atoms displaced as a result of development of cascade

The behavior of curves (Figs. 2 and 3) at increasing n' corresponds to transition from a regime of the linear cascades to a regime of thermal peaks.

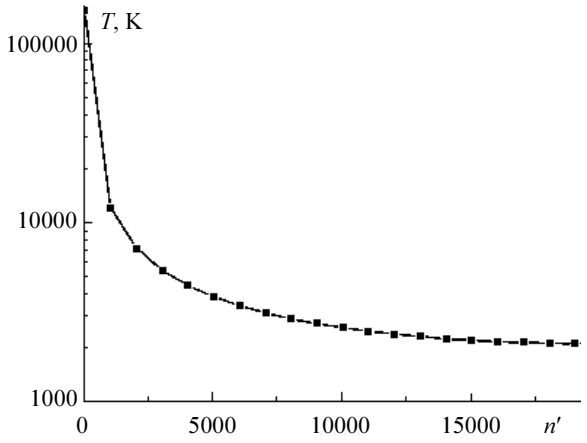

Fig. 3. Dependence of temperature of a cascade on number of displaced atoms

That is, at increasing of number of displaced atoms (that is equivalent to increasing of the energy inserted in volume V) the entropy grows and the temperature of volume V drops; the deviation of a many-body system from equilibrium in volume V decreases. Thus, the approach developed here integrates the linear cascade theory of a sputtering and patterns of thermal peak.

If number of quasi-particles n equal to number of collisions in a cascade with energy more than 100 eV (at smaller energies is not enough both section of excitation of colliding atoms, and section of go-ahead transmission of excitations) then $n < E_0/(2E_{cm} + 100\ \text{eV}) \approx 66$ (this is possible number of quantums at all energy levels in atoms of cascade).

Figure 4 shows dependence population of some level n from number of electrons at this level, counted according to (3).

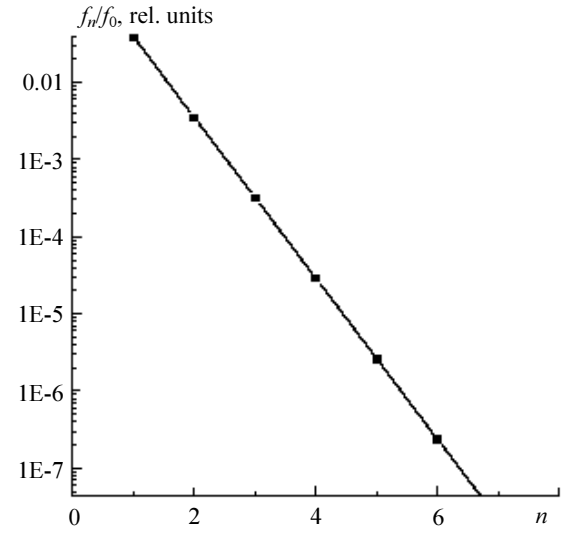

Fig. 4. Calculated probability of n level population dependence on number of electrons at this level: $kT_{cas} = 5$ eV, $kT_{ex} = 1$ eV, $\Delta E = 0.2$ eV, $E_1 = 4$ eV

It is visible that density of population of certain level sharply drops at increasing of electrons number at it. The estimate of total number of excited atoms ($n \approx 66$) in aggregate with dependence Fig. 4 matches at once to 3rd experimental facts: 1) to major number of lines in spectra of an ionic–photon emission; 2) to a small of a quantum yield ($\sim 10^{-4} - 10^{-3}$ quantum/ion) for separate transitions [10, 11]; 3) to common number of excited atoms among all sputtered (on the data [10] this quantity of ~ 10%, our calculations give $n/n' \sim 66/200 \sim 30\%$)

In Fig. 5 dependences of densities of levels population on temperature are shown at different temperature of quasi-particles (excitations).

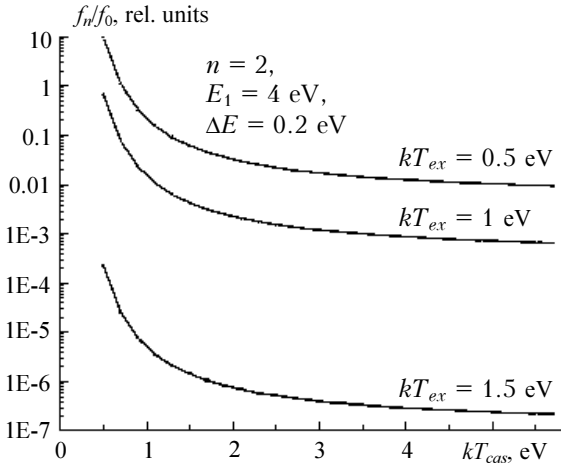

Fig. 5. Calculated probability of a population of level n dependence on cascade temperature at different temperatures of excitations: $n = 2$, $E_1 = 4.0$ eV, $\Delta E = 0.2$ eV

It is visible, that the population of levels drops both at increasing of temperature of cascade, and at increasing of temperature of excitations.

The greatest population is observed in field $T_{cas} < 2$ eV and $T_{ex} < 0.5$ eV. Such values T_{ex} correspond to simulated values of parameter T (from 1000 till 6000 K) in Boltzmann's distribution law when it is used as temperature for description of the relative population of levels in excited secondary atoms and ions for metals and alloys measured in experiment.

Were compared also the results of calculation and experimental data (taken of H.L. Bay's paper which translation is published in [10]) on levels population of sputtered Fe atoms at sputtered of iron. Good correspondence between the theory and experiment has been received. The same good correspondence between the theory and experiment [11] is observed at comparison of dependences population of a level from an excitation energy ΔE.

Thus, the probability of atoms excitation (3) well corresponds to all available experimental dependences on parameters which enter this formula.

Therefore, it is possible to expect that the probability of ions formation can be described with the help (3). To be convinced of it we have lead the following comparison. Multiply (3) on probability of ion neutralization near surface, considered within the framework of models of an electronic exchange [12–15]. Then we

shall receive for probability to register secondary atom in the ionized state after the termination of its interaction with a surface:

$$P^+ = f_0 \exp\left(-\frac{nE_1}{kT_e} + \frac{nE_1 - E_n}{kT_a} \right) \times \exp\left[-\frac{2\Delta(z_0)}{\gamma v_\perp} \right] =$$

$$= f_0 \exp\left[-\left(\frac{(n+1)E_1 + \Delta E}{kT_e} \right) + \left(\frac{nE_1}{kT_a} \right) - \frac{2\Delta(z_0)}{\gamma v_\perp} \right]. \quad (4)$$

At an arrangement (4) in comparison with (3) it is renamed $T_{ex} \to T_e$ and $T_{\text{cas}} \to T_a$ for convenience of the further comparison. Compare received formula (4) with analogous, called to take into account a heating of an electronic subsystem in the field of development of cascade within the framework of models of an electron exchange (formula (8) from [15]):

$$P^+ = \exp\left[-\frac{2\Delta(z_0)}{\gamma v_\perp} \right] +$$

$$+ \Gamma \left(\frac{\left| E_a'(z^*) \right|}{\gamma T_e} + 1 \right) \exp\left[-\frac{\left| E_a'(z^*) \right|}{T_e} \right], \quad (5)$$

where Δ is the half-breadth of a electron atomic level; γ is the constant describing an interaction length between atom and a surface; $v_\perp$ is the component of velocity of secondary atom perpendicular to surfaces; $E_a'(z^*)$ is the energy of level near to a surface on the reference distance z^* from it. It is easy to see, that practically all parameters included in (4) and (5) are same, and dependences P^+ from these parameters are equal. Exclusion makes parameter T_a: in (5) this parameter absence, however dependence P^+ from T_a in (4) same as well as P^+ from T_e in (5), therefore the indicated exclusion not basic. So (4) is possible to use for description of ions formation with the same success, as (5). About successful application of formula (5) for description of many regularities of secondary ion emission see [15].

3. Conclusion

In present article possibility of the description of atomic collisions cascades and excitation of atoms in cascades is shown with help of a formalism which based on base concepts of the nonequilibrium statistical physics. Within the limits of this approach formula (3) for calculation of probability of atoms excitation in collisions cascades corresponding to experimental dependences is offered. The concepts "temperature and entropy of the atomic collisions cascade" are entered into the theory of ionic sputtering for obtaining of formula (3).

The temperature and entropy of atomic collisions cascade in near-surface layer of solids at action by accelerated ions with energy about 10 keV are calculated. Empirical formulas (the most useful in the practical relation) for probability of secondary atoms ionization are theoretically proved.

References

[1] C.A. Andersen and J.R. Hinthorne, Sci. **75**, 853. (1972).

[2] V.S. Fajnberg and G.I. Ramendik, Zh. Anal. Khim. **46**/**2**, 241 (1991).

[3] M. Capitelli, *Nonequilibrium vibrational kinetics*, Berlin; Heidelberg; New York; London; Paris; Tokyo, Springer-Verlag, 1986, 395 p.

[4] N.N. Nikitenkov, *in Proc. Intern. Conf. Ion-Surface-Interaction*, Vol. 1, Moscow, 1995, 263 pp.

[5] N.N. Nikitenkov, *in Proc. Intern. Conf. Ion-Surface- Interaction*, Vol. 1, Moscow, 2001, 488 pp.

[6] N.N. Nikitenkov, *Processes at the ions sputtering of solid surface and energy-mass-spectrometry of the secondary ions*, Thesis of the doctor of phys. and math. sci., Tomsk, 321 (2007).

[7] V.A. Aleksandrov, A.S. Saburov, and G.M. Filimonov, Russ. Surface. X-ray, Synchrotron and Neutron Res. **4**, 99 (2002).

[8] Ch. Kittel, *Introduction to Solid State Physics*, 1956, 700 pp.

[9] Ju.V. Gott, *Interaction of particles with substance in plasma researches*, Moscow, Atomizdat, 1978, 271 pp.

[10] E.S. Mashkova, *Fundamental and applied aspects of solid surface*, Moscow, Mir, 1989, 349 p.

[11] V.V. Gritsyna, A.G. Koval, S.P. Gokov, and D.I. Shevchenko. Russ. Izvestiya RAS. Ser. Phys. **62**, No. 2, 829 (1998).

[12] H.G. Prival, Surf. Sci. **76**, 443 (1978).

[13] P.W. Anderson, Phys. Rev. **124**, 41 (1961).

[14] I.F. Urazgil'din, M.Yu. Gusev, D.V. Klushin, and S.V. Sharov, Phys. Rev. **B50**, 5582 (1994).

[15] I.F. Urazgil'din, Secondary ion emission. Russ. Izvestiya RAS. Ser. Phys. **60**, No. 7, 44 (1996).