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THE ROLE OF ENERGY DEPOSITION PROCESSES IN THE UNDERSTANDING OF LASER MICROPROBE ANALYSIS MECHANISMS

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Abstract

After emphasizing the role of local energy deposition as a common feature of many microanalytical techniques we focus our attention to laser ionization processes in mass spectrometry of solids. Enhancement of ionization in the case of high power density laser pulses can be rationalized in terms of hydrodynamic equations. The mechanism of shock wave generation and plasma ignition as well as excess energy absorption is demonstrated. Model calculations show that a one component - one dimensional (1C-1D) description can account for such important features of the laser ionization process as energy distribution of the produced ions. The role of classical absorption in the determination of plasma formation threshold is unfolded. Present efforts to relate the results with the fine structure of mass spectra are outlined. Targets are most commonly strongly inhomogeneous in practical microprobing. The induced plasma ignition concept is introduced in order to describe poorly reproducible mass spectra in these situations.

Key words: laser ionization mass spectrometry, laser microprobe, secondary ionization mass spectrometry, spark source mass spectrometry, energy deposition, energy distribution, plasma, hydrodynamic model, local thermal equilibrium

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Introduction

Local chemical analysis of a sample always includes as a step the microscopic excitation of the target with electromagnetic or particle beams; this step can also be regarded as a local energy deposition. Depending on the characteristics of the exciting beams we can classify the different microprobe techniques. Wavelength, intensity and duration of illumination determine which degree of freedom of the target spot can be excited with electromagnetic waves. According to this, we can distinguish between microfocused X-ray fluorescent analysis, resonant or non resonant multiphoton ionization, laser desorption, laser plasma ionization or simply microscopic spectrophotometry. Similar examples can be mentioned from the field of particle beams. The beams can consist of elementary particles such as electrons, protons, neutrons or of neutral atoms, molecules or their ions.

Further subdivisions can be made according to the detected species which carries the information about the chemical composition of the probed spot. In most of these techniques we can detect both electromagnetic waves and particles. We further confine ourselves to situations in which ions generated in the beam target interaction are detected. Consequently we also exclude such important methods as electron probe X-ray microanalysis (EPXMA), Rutherford backscattering (RBS), particle induced X-ray emission (PIXE), Auger electron spectrometry (AES).

In the forefront of the remaining techniques, we find the two most powerful microprobes: based on laser ionization (LIMS) and the secondary ionization mass spectrometers (SIMS), which achieve the highest sensitivity for elemental and isotopic analysis. Typical commercially available examples of LIMS microprobes are the LAMMA-1000 from Leybold Heraeus and the LIMA 3 from Kratos Analytical. The selection of microprobes is broader in the case of SIMS since the technique has a longer history. Just to name a few: IMS 4f from Cameca, MIQ-156 from ISA Riber, IMA-2A from Hitachi, etc.

Energy deposition and redistribution in the sample as a possible key to the understanding of these methods will be outlined in the first part of the paper. We give

special emphasis to the similarities between the processes involved in SIMS and LIMS techniques.

In the second part we will take a closer look at laser ionization, using a hydrodynamic description in rationalizing a large body of experimental observations available in the field.

The origin of the local energy deposition concept dates back to early investigations of radiation damage in solid materials. A comprehensive review of this subject including the early version of the temperature spike approach was written by Seitz and Koehler, (1956). The basic idea was that the high energy particle entering the target mediates its energy to the neighborhood through a collision cascade. The transferred energy heats up the surrounding of the track making atomic rearrangements possible.

This same idea reappears in the present literature of secondary and laser ionization in many ways, with the main difference that now we concentrate on the removed particles rather than on target damage.

There is another technique, the spark source mass spectrometry (SSMS) which can also be discussed in terms of energy deposition (Ramendik et al. 1987). Although it has never become a tool of local analysis, microscopic analytical capabilities have been demonstrated recently by Swenters et al. (1987), among others. The energy deposition concept has been used for a long time in the explanation of spark source mass spectrometric ion formation (see review by Ramendik et al., 1988).

According to the most probable mechanism in the sparking process, electrons, field emitted from the cathode, hit the surface of the anode depositing part of their kinetic energy gained from the electric field.

The deposited energy determines the basic features of the mass spectra. Part of the energy is devoted to the atomization of the electrode material. This process leads to morphological and chemical surface modifications as described by Verlinden et al. (1985) and by Swenters et al. (1986). Other parts of the deposited energy are used for ionization and for conversion into the kinetic energy of the atomized and/or ionized particles giving rise to ion energies as large as several hundred eV (see Fig. 1).

Ramendik et al. (1981) and Van Puymbroek et al. (1984) emphasized that the different energy distributions of the different ions combined with the limited energy acceptance of the spectrometer result in discrimination effects. Both this and the above mentioned electrode surface modification effect may account for the spread of relative sensitivity factors for different ionic species.

There is a difference of some 20 years between the introduction of the energy deposition concept in SIMS and LIMS in accordance with a similar time difference in the launching and practical use of the two techniques. So, it is most certainly useful to compare the results of both fields, since similarities may lead to benefits in the development of the less advanced LIMS theory. Because of this objective we will give a less detailed review of the SIMS literature, and will pay attention only to those aspects which can contribute to the understanding of LIMS as well. The reader interested more in SIMS is referred to the excellent book of Benninghoven et al. (1987).

To visualize the most important processes relevant in SIMS and LIMS based microprobes we first briefly describe the steps of local energy deposition in these situations. This part will be followed by the short review of the existing models. Introduction, solution and discussion of our hydrodynamic model can be found afterwards.

Steps of local energy deposition

Before any interaction takes place between the sample and the probing beam the situation is obvious. We have an energetic beam and a solid sample as it is prepared for investigation. After the analysis has been done the situation is simple again. The beam is partly absorbed, reflected or transmitted, the sample is more or less damaged and part of it is emitted in the form of neutral and/or charged particles.

There is a large body of investigations devoted to particle removal, redistribution and implantation in general. These processes acquired some technological significance and their application span from ion sputtering and ion implantation to laser annealing and laser drilling. Particle sputtering or particle ejection, however is not our main interest. It is only a prerequisite of free ion generation, which provides more or less fragmented cloud of the target material.

Since in mass spectrometry only ions can be detected the main task is to determine the nature, quantity and energy of the emerging charged particles. In order to do this we have to investigate what happens between the initial and final situation, namely the beam - target interaction.

For the understanding of this phase let us consider the typical parameters of the primary beams. In laser ionization Q-switched Nd-YAG, ruby and N_2 lasers are customary. Their wavelengths are in the range of $265nm < \lambda < 1060nm$ and pulse durations cover the region $5nsec < t_{pulse} < 50nsec$. Frequency doubling or quadrupling is widely used for shorter wavelengths. According to the delivered power density, Φ_0, the mechanism of ion formation ranges from simple laser desorption to plasma ionization. Usual values are $10^6 W/cm^2 < \Phi_0 < 10^{11} W/cm^2$, or in photon flux $\Phi_0/(h\nu) = 10^{24} - 5 * 10^{29} photons/(cm^2 sec)$.

In secondary ionization the primary ion beam usually consists of Ar^+, O_2^+, O^- or Cs^+. The kinetic energy of those particles is somewhere between 1keV and 20keV. Typical current densities are $10^{-10} A/cm^2 < i < 10^{-3} A/cm^2$, which correspond to ion fluxes in the range $i = 6 * 10^8 - 6 * 10^{15} ions/(cm^2 sec)$. Contrary to laser ionization we use here continuous excitation instead of pulses.

Comparison of dose densities used in the two cases

may be of interest. To carry out an analysis $5*10^{15}-2*10^{22} photons/cm^2$ or $10^{12}-10^{19} ions/cm^2$ are necessary.

In the beam target interaction, part of the energy carried by the beam is mediated to the target. The energy transfer itself is a multistep process.

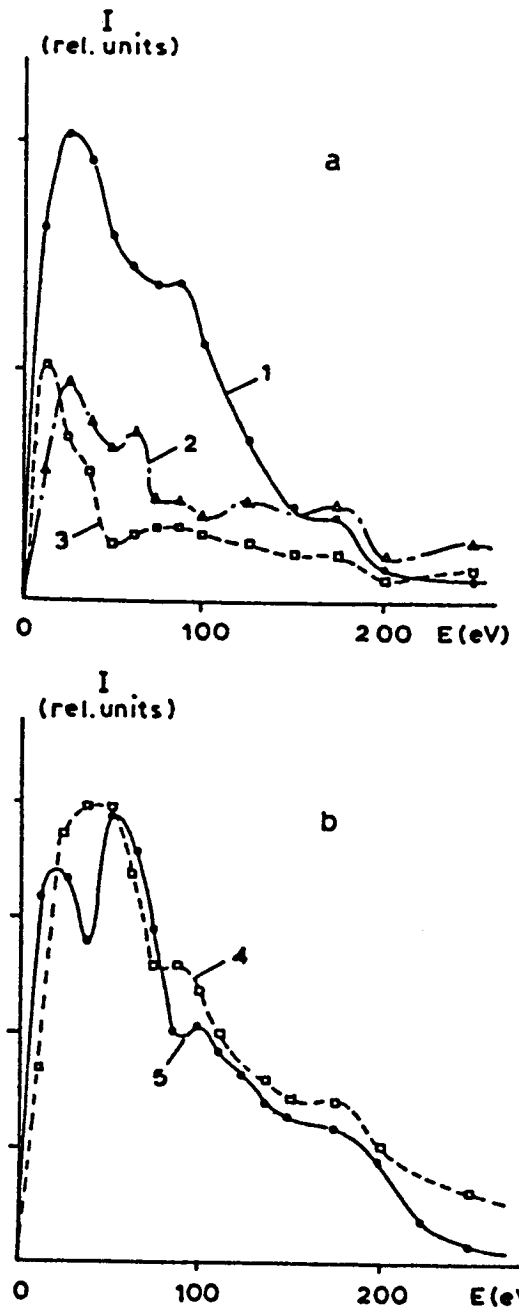

Figure 1. Kinetic energy distribution of ions formed in vacuum spark discharge under usual condition of SSMS. Tantalum probe was used against the International Geological Standard BM-1. The different curves correspond to: a/1-Si^+, a/2-Fe^+, a/3-Ti^+, b/4-O^+, b/5-C^+. The intensity of 2 and 3 on the Figure is increased by a factor of four for easier inspection (taken from the publication of Ramendik et al., 1981.).

Electromagnetic waves can excite some of the internal degrees of freedom of the material. Depending on the spectral range these are lattice or intramolecular vibrations or electronic transitions. Redistribution of this energy leads to heating, erosion, deformation and ionization. Photons, ions, electrons and neutrals are emerging from the interaction region. If the energy of the incoming photons coincides with one of the possible electronic transitions resonant ionization may take place. This is usually not the case unless special efforts are made. On the other hand, as ionization of the material increases due to normal absorption, resonant plasma absorption takes place at a certain critical electron density leading to strong heating of the electron gas. Contrary to resonant ionization this situation usually can be reached since particle density inside the solid is normally above the critical density.

Particle beams according to the widely accepted picture - see for instance Thompson (1981) - transfer their energy to the target by a collision cascade. Individual high energy ions penetrate the surface layers of the sample colliding consecutively with atoms. As a result of the collisions these atoms gain kinetic energy, electronic energy and there is a strong possibility of their ionization too. The deposited energy causes heating, deformation, sputtering of neutrals, photon, electron and ion emission processes.

Due to the usually high fluxes in both laser and ion beams non-equilibrium effects play a vital role during the interaction. For, example if we delivered the same amount of energy in laser ionization to a sample during $5sec$ instead of $5nsec$ we could hardly get any ionization at all.

The emitted ions, in the ideal case, should represent the local composition of the sample both qualitatively and quantitatively. In reality this is far from being true as is well known from the wide variations of the relative sensitivity factors. The outgoing ions can be produced from atoms, molecules and their fragments or clusters in singly or multiple charged forms. These different types are related to specific redistribution processes. Redistribution of the absorbed energy immediately after deposition accounts for the appearance of many of these ions either by fragmentation of atomic aggregates from the surface or by ion molecule or other reactions of the leaving particles. The general situation is schematically explained in Fig. 2.

Models of energy deposition and redistribution

In general, the energy loss of electromagnetic and particle beams can be treated in a quite similar way. In the case of light one usually can define a local absorption coefficient, $\alpha(x,t)$, which determines the local light power density, $\Phi(x,t)$, through an absorption law. The functional form of this law can be expanded in power series of Φ:

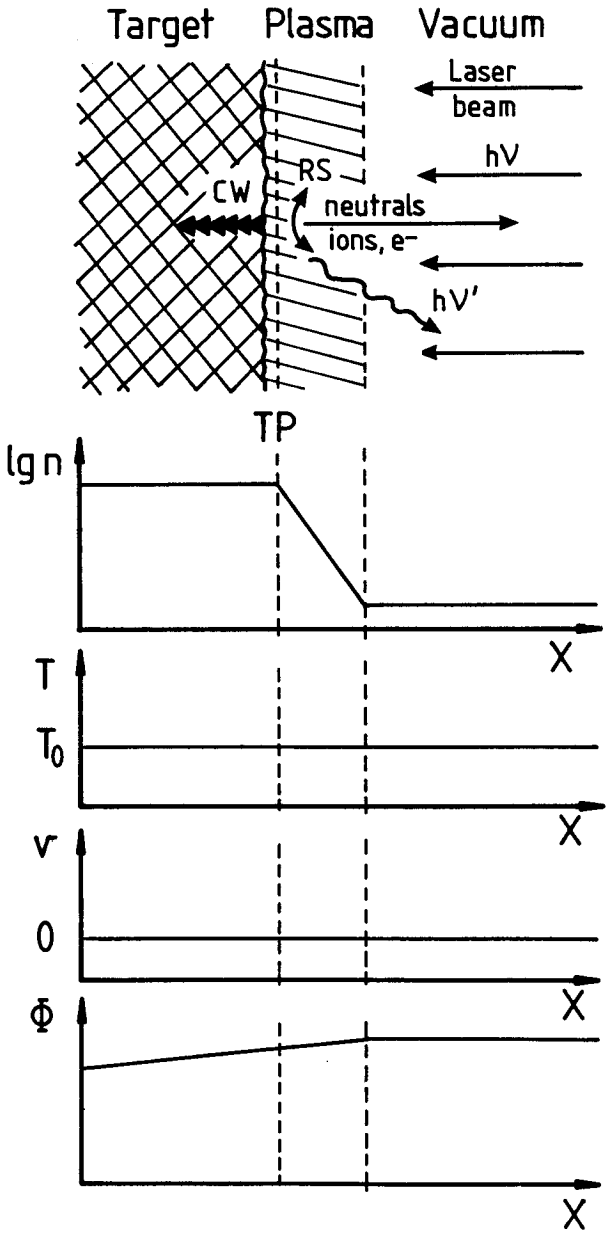

Figure 2. Schematic view of the laser beam - target interaction, together with the initial conditions of our hydrodynamic calculations. We emphasized some elementary processes occurring in the interaction region. Apart from sputtering and plasma formation, compression wave (CW) generation, reactive scattering (RS) of the plasma components and radiative transitions ($h\nu'$) in the plasma are displayed. The initial surface of the solid is called target plane (TP). At the lower part of the Figure initial spatial distributions of particle number density, n, temperature, T, velocity, v and light power density, Φ are shown.

$$\frac{\partial\Phi(x,t)}{\partial x} = -\alpha(x,t)\Phi(x,t) - \beta(x,t)\Phi^2(x,t) + ..., \quad (1)$$

where $\beta(x,t)$ is the first nonlinear coefficient. At normal light intensities only the linear term is important and the absorption law has the form:

$$\Phi(x,t) = \Phi_0 exp\left[-\int_x^\infty \alpha(x',t)dx'\right], \quad (2)$$

where the light propagating along the x axis has initial intensity, Φ_0.

Since non-linearity is usually preceded by evaporation and strong ionization of the material we may estimate its relevance on the basis of non-linear plasma absorption. Non-linear absorption becomes only important if the oscillation energy of the electrons in the plasma, E_{osc}, is comparable to the thermal energy, kT. Using the estimation of E_{osc} (Hora, 1979, p. 72):

$$E_{osc} = \frac{\Phi_0}{2cn_{cr}}, \quad (3)$$

so the laser intensity where non-linear effects start to play a role is:

$$\Phi_0^{thr} = 2ckTn_{cr}. \quad (4)$$

Here n_{cr} is the critical electron density leading to resonant plasma absorption:

$$n_{cr} = \frac{m_e\omega^2}{4\pi e_0^2}. \quad (5)$$

In the case of a ruby laser evaluating Eq. (4) provides: $\Phi_0^{thr}\ (W/cm^2) = 2.5 * 10^9\ T\ (K)$. To achieve some ionization at least $1000K$ is necessary, therefore the non-linear effects turn on at $\Phi_0^{thr} = 2.5 * 10^{12}\ W/cm^2$. This is well beyond the interesting region for laser ionization.

Energy loss of particle beams can be treated with the so called nuclear and electronic stopping power of the target, S_n and S_e:

$$\frac{d\,E}{d\,x} = -n_a(S_n(E) + S_e(E)), \quad (6)$$

where n_a denotes the number density of atoms in the target. The functions $S_n(E)$ and $S_e(E)$ are related to the scattering cross sections of target atoms and are subject of laborious calculations. They are expressed in the form of power functions of fractional order (Benninghoven et al., 1987, p. 20-31). It is worthwhile to mention that contrary to laser ionization, secondary ionization is based on strongly non-linear energy deposition processes.

After identifying the amount of energy loss in the

beam we would like to know the fate of the deposited energy in the target. There are numerous different investigations concerning the members of a very complex family of elementary events during the energy redistribution process. We focus our attention only on the approaches which are relevant to microprobe techniques.

Two limiting cases can be separated in both methods. If gentle excitation is used the system doesn't deviate very much from equilibrium and thermodynamic control of the events can be observed. At low energy particle bombardment and at low laser power densities the generated ions will exhibit Maxwellian kinetic energy distribution (Van Der Peyl et al. 1984, Schäfer and Hess, 1985).

In the other limit of extremely severe excitation where strong non-equilibrium processes arise, the control is rather kinetic. As a consequence new mechanisms of ion formation are commonly considered. It is well known, for example, that enhancement of particle yields in the case of high mass and/or high energy primary particles (Ahmad et al. 1980) and high power density light pulses (Conzemius and Capellen 1980) is found. One of the interesting challenges in the field of secondary and laser ionization is undoubtedly the explanation of these effects.

The kinetic energy spectrum of the generated ions in the case of intense excitation also shows remarkable irregularities. Strongly non-Maxwellian behavior

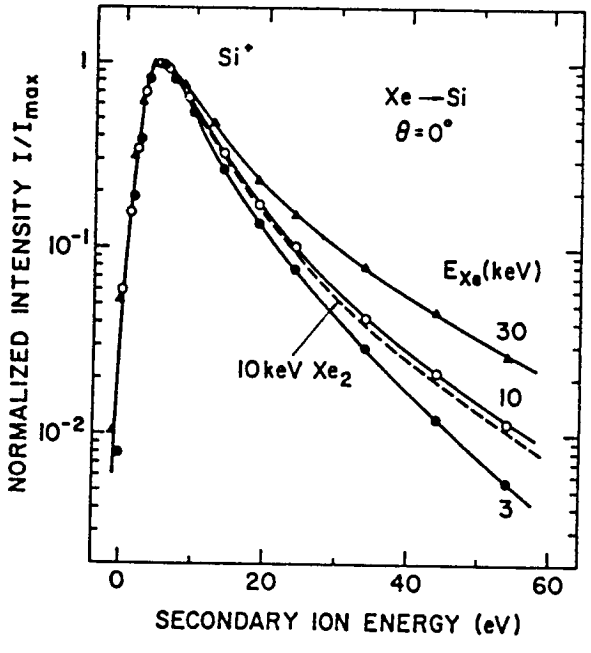

Figure 3. Energy spectra of Si^+ for Xe^+ impact at normal incidence at three different xenon energies. The dashed line corresponds to 10keV Xe_2^+ bombardment. (Figure is from Wittmaack, 1979)

is demonstrated in Fig. 3 for SIMS and in Fig. 5 for LIMS. In the second case the high power density laser pulse induces ion production and the ion kinetic energy distribution exhibits a strong peak in the $100eV$ region. Similar observations for ions, just as for neutrals (Ahmad et al. 1980, Husinsky et al. 1980, Mauney and Adams, 1984, Michiels et al. 1984) draw increasing attention to alternative descriptions capable of predicting these features.

In order to see the possibilities for the general description of laser ionization capable of handling non-Maxwellian ion generation let us have an overview of the existing models having this objective in mind. Three separate classes of the previous models can be distinguished depending on the level of description. The phenomenological, the kinetic and the molecular levels can be clearly separated, although mixing of the levels in one model is also quite frequent. It is necessary to emphasize that this classification is based on differences in the machinery used to describe the processes rather than on differences in the mechanisms investigated.

Phenomenological models

The so called phenomenological models are mostly used in the early stage of investigation since no microscopic knowledge of the processes involved is necessary. In fact the earliest models based on the ***spike concept*** belong to this group.

The idea is that an energetic beam causes a strong excitation of the target localized in space and time. This excitation can be vigorous heating, permanent displacement of particles, elastic deformation, ionization or any combination of these. Afterwards the excitation spreads radially from the point of generation and this process can be described with the radial form of conservation laws. The energy density, $e_{ini}(\underline{r})$, deposited initially spreads in the target according to:

$$\frac{\partial e}{\partial t} = \nabla \kappa \nabla e, \qquad (7)$$

where $\kappa(e)$ is the thermal conduction coefficient of the material, usually a nonlinear function of the energy density. At every point which reaches the necessary energy density ions are generated and their yield can be calculated using the absolute rate theory of Eyring (Glasstone et al., 1941) for example.

The conventional form of the spike theory deals only with conductive energy transport. This is quite adequate in the case of low energy ion bombardment or low intensity laser desorption. According to the arguments of Sanders (1980), based on spike theory, 6 keV Xe^+ bombardment of Au and RbBr targets doesn't lead to the development of shock waves since coherent motion in the collision cascade is absent.

The ***hydrodynamic models*** focus on the transport of particle momentum and energy as a continuum during and following energy deposition. Their machinery is

based on conservation laws of these quantities in more or less general form. However, the necessary transport coefficients are usually derived from statistical theories. Since plasma formation in the medium and high incoming flux regions is confirmed, in these cases the transport theory of Spitzer (1962) is widely applied. Details of the hydrodynamic approach will be outlined in below. Here we mention only that hydrodynamic models are well suited for handling strongly non-equilibrium cases.

The best known and most widely used theory of all is the *local thermodynamic equilibrium or LTE theory.* Although it is deliberately used in both SIMS and LIMS (Andersen 1975, Newbury 1980, Castaing and Slodzian, 1981, Odelius et al. 1985, Fürstenau 1981, Haas et al. 1981, Eloy 1985, 1986) for the estimation of ion production its popularity is probably more due to the ease of handling than to coherent arguments. A rigorous description of the model was given by Drawin (1971).

The idea is that from the point of view of ion generation complete thermodynamic equilibrium is reached after the interaction. The only exception is the equilibrium of the target with the perturbing species. Even if we forget about the demonstratedly non-Maxwellian energy distribution of the generated ions (see for instance Benninghoven et al. (1987) for SIMS or Tallents (1980, 1981), Mauney and Adams (1984) and Michiels et al. (1984) for LIMS) the concept contains controversy in itself: extreme non-equilibrium situations are described by an equilibrium theory.

The general law of chemical equilibrium for reactions of the type:

$$AB \rightleftharpoons A + B, \tag{8}$$

with the net energy change, E_{AB}, can be written in the form:

$$\frac{n_A n_B}{n_{AB}} = \\ = \frac{Q_A Q_B}{Q_{AB}} \left(\frac{m_A m_B}{m_A + m_B} \right)^{3/2} \frac{(2\pi kT)^{3/2}}{h^3} exp\left(-\frac{E_{AB}}{kT} \right). \tag{9}$$

where n_A, n_B, n_{AB} denote the number densities of species A, B, and AB. Q_A, Q_B, Q_{AB} and m_A, m_B, m_{AB} are the corresponding internal partition functions and particle masses respectively.

In the case of ionization processes this formula is simplified to the Saha - Eggert equation and solved in order to provide ionic yields. In many cases E_{AB} is simply identified as atomic or molecular ionization potential, I_p, although more realistic ionization values can be obtained if collective effects in the plasma are taken into account (Drawin, 1971, p. 94-95):

$$E_{AB} = I_p - \frac{e_0^2}{\lambda_D}, \tag{10}$$

where e_0 is electron charge and λ_D is the Debye screening length:

$$\lambda_D = \left(\frac{kT}{4\pi n_e e_0^2} \right)^{1/2}. \tag{11}$$

Here λ_D depends on n_e the electron density.

Similarities of the mass spectra obtained by SIMS, fast atom bombardment (FAB), heavy ion induced desorption (HIID), ^{252}Cf fission fragment induced desorption (FIID), infrared and ultraviolet LIMS led Krueger (1983) to the idea of relating their main features to energy deposition and redistribution processes. He established a theoretical model utilizing a *non-equilibrium statistical description* of the phase transition processes, thought to be the common denominator in all these analytical methods. Although the approach is very general and the method is elegant, the large number of unknown parameters makes it difficult to apply the model in real situations.

Another model is based on the *space charge limited current (SCL) theory.* The basic idea is that charge extraction from a plasma cloud in an electric field is limited by the stationary equilibrium between the external field and the internal field generated by the displacement of electron and ion clouds. The extent of this displacement is in the order of λ_D and the current density, j_{SCL}, which can be extracted from the cloud is limited to:

$$j_{SCL} = \frac{1}{9\pi} \left(\frac{2e_0}{m_i} \right)^{1/2} U_a^{3/2} d^{-2}, \tag{12}$$

where U_a is the extracting potential difference acting on a distance d (see for instance Wilson and Brewer, 1973). So far the application of this theory has been limited to the description of low power density laser ionization (Van der Peyl et al., 1984).

Kinetic models

In situations where individual events governing the distribution of position and velocity of the particles cannot be neglected the phenomenological equations have to be replaced by the Boltzmann type equations (Sigmund, 1969):

$$\frac{\partial f(E,r)}{\partial r} = \\ = n \int [f(E,r) - f(E - \Delta E), r)] + n S_e(E) \frac{\partial f(E,r)}{\partial E}, \tag{13}$$

where $f(E,r)$ is the probability distribution of the primary ion pathlength in the solid, r, at E initial kinetic energy. Typically non-equilibrium processes are treated with this approach.

Individual transitions certainly govern the events in ion bombardment experiments as can be expected from the relatively low incoming flux of ions. Since the basic work of Sigmund (1969) sputtering of solids by ion beams is handled by this formalism quite successfully. He describes the energy transfer to the particles of the target by the concept of ***collision cascades***. A cascade is a sequence of mainly elastic collisions between the energetic particles and the atoms of the target.

Sigmund's theory is successful in many applications ranging from ion sputtering through secondary ionization to ion implantation. It is also worked out for different types of targets, such as amorphous and polycrystalline solids and single crystals. As one of the results of the theory it was possible to calculate the spatial distribution of deposited energy and relate it to the quantity of recoiling atoms and to the low energy part of their kinetic energy spectrum in the case of high primary energy particles. Littmark and Sigmund, (1975) extended the energy deposition concept to the deposition of another conserving quantity: the deposition of momentum and calculated the mean velocity of the secondary particles.

The frontiers of the cascade theory are marked by the non-linear collision cascade regime and by the extreme difficulties in the case of complex molecular targets (Kidwell et al. 1987). A cascade is called linear when the density of recoil atoms is sufficiently low to take the events in two different cascades independent. If this condition is not fulfilled the solution of Eq. (13) raises enormous problems and the spike approach is more adequate (Sigmund 1984).

In the case of more and more interesting complex molecular targets the problem is that the conventional formalism of the cascade theory is based on the motion of individual atoms. Although generalization of the model for simple two- or three-atom molecular ion formation was also possible (Gerhard 1975) more complex targets are still not within its scope.

In the case of several molecular samples the gas collision model (Sunner et al. 1986,1988) gives satisfactory results. It is based on the kinetic description of ion-molecule reactions in the dense plasma and capable of predicting secondary ion currents in FAB experiments. This theory is a non-equilibrium complement of the LTE model and in the long residence time limit its results should converge to LTE results.

Recently Johnson (1987) applied the energy deposition concept in the description of ionization spectra of large organic molecules by high energy ions. He addressed the problem of ion generation from organic targets by high energy ions having energies in the order of MeV. In his model the deposited energy partly expands the solid and partly causes permanent bond ruptures leading to fragment ion formation.

Kinetic modeling of events in laser ionization has not been applied so far. Comparison of the incoming fluxes in SIMS and LIMS (see above) explains why: the photon flux is about 14 orders of magnitude higher than the bombarding ion flux, therefore tracing individual absorption events seems hopeless.

Molecular models

In the description of particle beam target interaction it is getting more and more widespread to treat the problem with computer simulation of a large number of scattering events. Here again, the number of elementary events in the case of laser ionization is many orders of magnitude higher. So, it is not promising to carry out similar investigations at the present state of the computer art. Still there are interesting aspects of these simulations worth mentioning in the context of energy deposition.

In the common form of these Monte Carlo simulations, the incoming particle is supposed to travel along a straight line until a collision changes its direction. The energy loss of this particle and consequently the energy transfer to the target is calculated in two parts. At the elastic collisions, the ion transfers energy to the nucleus of its colliding counterpart and between the elastic events inelastic encounters take place with the surrounding electrons.

Primary particle and recoil atom trajectories can be traced, even visualized on the computer display until they completely lose their kinetic energy inducing secondary processes accompanied by the redistribution of the deposited energy. There exists a broad selection of Monte Carlo codes with a wide variety of purposes and special handling of the problem. (The different programs are sometimes identified by acronyms: MARLOWE, Robinson and Torrens, (1974), TRIM, Biersack and Haggmark, (1980), COSIPO, Hautala 1984.)

It is possible with these programs to calculate the spatial distribution of deposited energy related to nuclear and electronic processes, although mainly for simple atomic particles having no internal structure or degrees of freedom. For example, detailed investigations were carried out to determine the dependence of the sputtering yield on the surface deposited energy (Thompson and Johar, 1980). More complex targets are treated by substituting an artificial "effective" solid of simple character instead of the original (Whitlow et al. 1987).

Unlike in laser ionization, under SIMS conditions the incoming particle flux frequently makes it possible to separate the effect of individual cascades. Therefore, the target atoms are in their normal state prior to the interaction with a primary particle or with its recoil atom. Comparing the photon and particle fluxes given above, this is obviously far from true in LIMS. Most probably this basic difference has made it impossible to use Monte Carlo simulations in laser ionization studies and will remain an obstacle for some time.