Energy distributions of Ga\(^+\) and In\(^+\) secondary ions sputtered from A\(^{III}\)B\(^{V}\) compound semiconductors by noble gas ions: Mass-dependence of the high-energy yield on the second component (P, As, Sb) of the compounds

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Abstract

Experimental and simulated energy distributions of Ga\(^+\) and In\(^+\) secondary ions produced by 4 keV Ne\(^+\), Ar\(^+\) and Kr\(^+\) bombardment of the A\(^{III}\)B\(^{V}\) semiconductors (GaP, GaAs, GaSb, InP, InAs and InSb) are reported. The measurements were carried out for a wide range of initial energy (up to 1000 eV) in a small solid angle along the surface normal, without applying electric field to extract the ions into the mass-energy analyser. It is shown that the energy spectra are complex, with evident high-energy hump, whose relative intensity increases with the mass of the second component (P, As, Sb) of the compound. The Sigmund–Thompson distribution cannot fit reliably these data, and a satisfactory approximation of the measured spectra was obtained with a sum of two decaying exponential functions to describe the contribution of both, the isotropic linear collision cascades and the outward knock-on atoms. The experimental results are compared with simulations based on the MARLOWE computer code.

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1. Introduction

It is usually assumed that the kinetic energy distribution \(N(E)\) of sputtered particles is reasonably well characterized by the Sigmund–Thompson formula [1–3]

\[
N(E) \propto \frac{E}{E + E_b} g(E + E_b), \quad (1)
\]

where \(g(E) \propto E^{-2}\) implies an isotropic distribution of recoiling atoms produced in linear collision cascades inside the solid, and \(E_b\) stands for the height of a planar surface potential barrier or a surface-binding energy. Approximation (1) is justified only if the collision cascade anisotropy can be neglected. This is the case for recoils with energies well below the maximum energy transfer, \(T\),...
where $E$ and $E_0$ are respectively the energies of the recoil and the projectile, and $M$ and $M_0$ are the corresponding masses. Deviations from the Sigmund–Thompson formula are expected if this condition fails (see, e.g. [4–6]). A number of experiments (see, e.g. [7–14] and references cited therein) have shown that the energy distribution (ED) of sputtered ions reveals complicated, non-monotonic fall-off, occasionally with an evident high-energy hump. The presence of a particular mechanism of secondary ion formation [15,16], which prevails at the high-energy range (greater than 100 eV), is considered usually responsible for such a structure.

Recently, Goehlich et al. [17,18], using pulsed laser-induced fluorescence technique, have measured EDs of sputtered aluminium atoms with pronounced double-shaped structure depending on the direction of particle emission. High-energy peak in the distributions was explained by a contribution of primary knock-on atoms, and a satisfactory analytical representation of the measured data is obtained by a distribution of recoiling atoms involving two decaying exponential functions, namely

$$g(E) = A \exp(-E/E_1) + B \exp(-E/E_2).$$

In the present study, the kinetic energy distributions of Ga$^+$ and In$^+$ secondary ions resulting from the noble gas ion bombardment of different A$^{III}$B$^V$ compound semiconductors, where A-component is gallium or indium, and B-component is phosphorus, arsenic or antimony, have been examined by energy-resolved secondary ion mass spectrometry [9,19–21] and by computer simulations based on the MARLOWE computer code [10,22–24].

EDs of secondary ions, their high-energy tails in particular, are sensitive to the mechanisms of transfer of kinetic energy from the primary ions and from the surrounding atoms to the particle to be emitted. Pure, single-crystal A$^{III}$B$^V$ semiconductors may be considered as model binary systems, and a thorough study of the energy spectra of Ga$^+$ and In$^+$ as function of the mass of the second component (P, As, Sb) of the compounds should be most helpful in assessing the ballistic contribution to the secondary-ion yield. To the best of our knowledge, there are no reports published in the literature, neither experimental nor computer simulations, that are devoted to such a comprehensive study.

2. Experimental

The measurements were carried out by means of a dedicated instrument based on standard commercial components. Details of the system have been reported in our previous publications [9, 19]. Briefly, the Hiden EQS 1000 Mass Energy Analyser, a pivotal element of the installation, combines a high transmission electrostatic energy analyser and a quadrupole mass-spectrometer. It applies to measure energy-resolved mass spectra and mass-resolved EDs of both sputtered and scattered ions. At typical passing energy of $E_a = 80$ eV the energy resolution $\Delta E_a$ is less than 3.0 eV full-width at half maximum (FWHM), and the mass resolution $\Delta M$ (FWHM) is $\approx 0.75 \pm 0.05$ amu in the mass interval of 1–1000 amu. In the measurements described below we have used an electron-impact ionisation gas ion source IQE 12/38 by Specs [25].

The noble gas ion projectiles (Ne$^+$, Ar$^+$, Kr$^+$) with bombarding energy of 4 keV were directed at a fixed incident angle $\psi = 30^\circ$ with respect to the surface plane. The ion current density was 0.15 mA/cm$^2$ or less, and the raster-scanned primary beam was sputtering a target area of about 1 mm$^2$. A 75% electronic gating of the registration system was applied during the collection of the energy spectra.

All measurements were carried out: (i) at “in-plane” geometry, collecting the ions along the surface normal with a constant total acceptance angle of $\approx 1.5^\circ$; (ii) with the sample at a fixed (ground) potential, without applying accelerating electric field to extract secondary ions into the...
mass-energy analyser; (iii) under steady-state bombarding conditions, with secondary-ion intensities constant as a function of the primary-ion dose \((D \geq 10^{16} \text{ ions/cm}^2)\).

The samples probed were single-crystalline (100), \(n\)-type \((n \sim 10^{16} - 10^{18} \text{ cm}^{-3})\) compound semiconductors manufactured in the Institute of Microstructures Physics, Russian Academy of Sciences (N. Novgorod).

Mass-resolved energy spectra of Ga\(^{+}\) and In\(^{+}\) secondary ions were measured at energies ranging from 2 to 1000 eV by a digital scan with variable energy step (2–50 eV) and dwell time (up to 10 s) depending on the signal intensity. Final ED data were averaged over 4–6 successive measurements. The ion intensities were corrected for dead-time losses of an ion-counting secondary electron multiplier (SEM) by applying a correction procedure similar to that described in [26].

3. Computer model

Modified MARLOWE sputter code v.12 was used for the computer simulations in this study. Since the experimental data are measured in a steady-state regime, we considered that all target anisotropy effects have been destroyed. Although some modification of the stochiometric composition of the compounds under ion-beam bombardment is expected, it was not taken into account. Our recent quantification of the highly irradiated GaSb sample by mass-resolved ion-scattering spectrometry [27] has revealed that for bombarding energies \(E_0 > 1 \text{ keV}\) the relative surface composition of the sample is close to the stochiometric ratio.

We applied here most of the standard assumptions of the MARLOWE code [22,23] for modelling atomic collision cascades in solids. These include Molière interatomic potential to describe the elastic part of the interaction between the particles (with shortened by a factor of 0.8 Firsov screening length) as well as equi-partitioned contribution of local and non-local inelastic losses for the primary ions. Our code follows somewhat more parameters of the collisions then the original version (for details, see [10]). The number of simulated ion trajectories followed by ion induced collision cascades was \((1\text{–}2) \times 10^6\).

The surface-binding energy, \(E_b\), is not a well-defined parameter for such compounds, particularly under dynamic ion-beam bombardment. Half of the standard heat of atomisation [28] are taken to represent \(E_b\) here, viz. 3.49 eV (GaP), 3.34 eV (GaAs), 2.97 eV (GaSb), 3.42 eV (InP), 2.80 eV (InAs) and 2.73 eV (InSb).

4. Results and discussion

Prior to main measurements, the samples were sputter-cleaned. The surface composition was monitored by collecting the mass spectra of both positive and negative secondary ions. No ion species (atomic, molecular, etc.), which could mass-interfere with Ga\(^{+}\) or In\(^{+}\) isotopes, have been observed on the level of the instrumental sensitivity for the samples probed.

Before going further, we have to note some assumptions accepted in this study. We suggest that the signal \(S\) of singly charged positive secondary ions due to the \(k\)-isotope of the \(i\)-component of the sample may be written in general form as

\[
S_k(E) = IY_i(k)N_i(E)^kP_i(E)^k F_i(E)^k 
\]

where \(I\) is the primary-ion current, \(Y_i\) is the total sputtering yield, \(N_i(E)\) is the flux of sputtered neutral atoms, \(P_i(E)\) is the ionisation probability, \(F_i(E)\) is an apparatus factor including the analyser transmission and the detector efficiency, \(\gamma_i\) is the isotope abundance, \(C_i\) is the relative concentration, the superscript \(k\) of all factors indicates the mass of the isotope ions.

The validity of such factorisation is currently being debated [29], but nevertheless it remains generally accepted for describing secondary-ion yields (see, e.g. [30]). Under our particular experimental conditions, listed in Section 2, the ED measurements should be considered as angular-resolved with fixed exit, therefore we ignore any angular dependence in Eq. (4). For given type of secondary ions the transmission through the EQS 1000 Probe is practically independent of initial ion energy (above \(E = 3\text{–}5 \text{ eV}\)). This conclusion holds true only for quasi-paraxial, not too diverging
particles, as proved by the results of our ion-trajectory calculations performed by the SIMION 3D code [31]. The detector efficiency is approximately constant in the investigated energy range for identical ion species of the same mass and charge, since they impinge upon the first dynode of the SEM with the same energy (velocity), independent of their emission energy.

The last, but not least assumption is related to the ionisation probability of Ga$^+$ and In$^+$ secondary ions or, rather, to their energy (velocity) dependence. Šroubek and Oechner reported [32] that for GaAs sample, bombarded by He$^+$ and Xe$^+$ projectiles with energies between 0.5 and 4 keV, the ionisation probability of Ga$^+$ secondary ions was not sensitive to their velocity. Our ED measurements of Ga$^+$ and In$^+$ isotope ions [33] confirmed this result as well; it was found that for $E > 80–100$ eV isotope fractionation, i.e. deviation of the measured isotope ratio from the “true” isotopic abundance, is energy-independent function for all compounds studied. Keeping these considerations in mind, we can simplify Eq. (4) and assume that in the high-energy range $S(E) \propto N(E)$.

Both experimental and simulated kinetic energy distributions of $^{69}$Ga and $^{115}$In particles sputtered under Ne$^+$ bombardment of A$^{III}$B$^V$ semiconductors are shown in Fig. 1. The EDs measured for bombardment of a given target by 4 keV Ar$^+$ and Kr$^+$ are similar to those recorded for Ne$^+$ projectiles. All curves are scaled to the yield at energy $E = 100$ eV, considered well exceeding $E_b$ to avoid the uncertainty involved with the surface-binding energy. As mentioned above, the EDs of the secondary ions above 100 eV can be considered corresponding to the energy distributions of sputtered neutrals. No corrections of the emission energies due to image potentials or other surface barriers [34,35] were introduced in our study.

The graphs presented in Fig. 1 display evidence of high-energy humps present in both $^{69}$Ga$^+$ and $^{115}$In$^+$ energy distributions. The intensity of this feature depends on the mass of the complementary component of the compounds. On the contrary, the most probable energy, $E_{mp}$, i.e. the energy corresponding to the peak of the EDs, is equal to $18 \pm 2$ eV for all of the experimental spectra. The width (FWHM) of the distributions, $\Delta E_{0.5}$, is $16 \pm 2$ eV, and it is a mass-independent parameter too. Two more parameters of the measured EDs are summarised in the table: the average energy, $E_{avr}$, estimated for the energy range of $E = 2–1000$ eV with a step of 1 eV, and the scaling intensity, $I_{scal}$, measured at $E = 100$ eV.

The increase in mass of the second component, from phosphorus (31 amu) to arsenic (75 amu) and, next, to antimony (121.8 amu), facilitates the reversal of the initially inward momentum back toward the surface, and it results in higher average...
energy of the ejected particles for emission of both Ga and In recoiling atoms (see Table 1). For all compounds the values of $E_{\text{avr}}$ reveal slight growth with increase of the projectile mass from $M_{\text{Ne}} = 20$ amu to $M_{\text{Ar}} = 40$ amu and $M_{\text{Kr}} = 83.8$ amu.

Compared to the measured secondary ion energy spectra, the simulated distributions of the sputtered (neutral) atoms peak at lower energies, from 3 to 5 eV for the chosen $E_b$. Within the limited number of simulated trajectories the average energy of these EDs cannot be distinguished reliably. We need to point out that for the computer simulation distributions we have used 3° acceptance angle in order to obtain reasonable statistics. This angle is larger than the experimental angle (1.5°), that may smear out some distinct high-energy features of the calculated EDs. The number of sputtered particles with kinetic energies over 1000 eV, recorded in the simulations, is steadily increasing from P to As and Sb, e.g. 1.8, 3.6 and 4.8 ($\times 10^{-6}$ atoms/ion) correspondingly for GaP, GaAs and GaSb exposed to the bombardment of 4 keV Ne$^+$. Similar results have been obtained for In-based compounds. These facts are consistent with the high-energy features referred to in the experimental data.

It is known [1,36] that the abundance of secondary ions of a given energy, hence the average energy, is proportional to $T$, the maximum transfer of energy from a primary ion to a target atom in head-on collisions. Strictly derivation of an analytical expression, involving dependence of the $T$-parameter versus mass of the second component of the compounds, is a difficult task since a variety of possible collision sequences resulting in emission of recoiling atoms can occur. One can reasonably suggest that both primary and secondary knock-on atoms (PKA and SKA, see [37]) contribute to the high-energy tail of the EDs (Fig. 1), which by no means can be described by power law dependence, $E^{-2}$, as predicted by the Sigmund-Thompson formula.

According to the formalism proposed in [17,18], we can fit the energy spectra of recoiling atoms inside the solid by superposition of two exponential functions and obtain the following analytical expression:

$$N(E) \propto \frac{E}{E + E_b} \left\{ A \exp \left[ - \frac{(E + E_b)}{E_1} \right] + B \exp \left[ - \frac{(E + E_b)}{E_2} \right] \right\} = N_1(E) + N_2(E),$$

where $N_1(E)$ stands for the ED of direct knock-on atoms and $N_2(E)$ is a contribution of the isotropic linear collision cascades. An application of such an approach to the fitting of the energy spectrum of $^{69}\text{Ga}^+$ ions sputtered from GaSb sample by 4 keV Ne$^+$ projectiles is presented in Fig. 2. The values of the fitting parameters are as follows: $A = 2.146 \pm 0.145$, $B = 103.1 \pm 3.63$, $E_1 = (142 \pm 11)$ eV and $E_2 = (11.32 \pm 0.21)$ eV. Surface-binding energy of 2.97 eV was assumed. A good conformity between experimental, simulated and model distributions is obtained for emission energies $E > 20$ eV. The low-energy part ($E < E_{\text{imp}}$) of the EDs is influenced to a great extent by velocity-dependent ionisation/neutralization processes and

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sec. ion</th>
<th>$^{69}\text{Ga}^+$</th>
<th>$E_{\text{avr}}$ (eV)</th>
<th>$I_{\text{scal}}$ ($\times 10^3$ cps)</th>
<th>$^{115}\text{In}^+$</th>
<th>$E_{\text{avr}}$ (eV)</th>
<th>$I_{\text{scal}}$ ($\times 10^3$ cps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaP</td>
<td>$^{69}\text{Ga}^+$</td>
<td>38</td>
<td>12.1</td>
<td>43</td>
<td>40</td>
<td>11.2</td>
<td>11.2</td>
</tr>
<tr>
<td>GaAs</td>
<td>$^{69}\text{Ga}^+$</td>
<td>49</td>
<td>41.4</td>
<td>53</td>
<td>40</td>
<td>40.6</td>
<td>33.2</td>
</tr>
<tr>
<td>GaSb</td>
<td>$^{69}\text{Ga}^+$</td>
<td>87</td>
<td>20.2</td>
<td>100</td>
<td>23.6</td>
<td>23.3</td>
<td>10.0</td>
</tr>
<tr>
<td>InP</td>
<td>$^{115}\text{In}^+$</td>
<td>40</td>
<td>9.12</td>
<td>44</td>
<td>11.2</td>
<td>11.2</td>
<td>11.2</td>
</tr>
<tr>
<td>InAs</td>
<td>$^{115}\text{In}^+$</td>
<td>49</td>
<td>19.3</td>
<td>55</td>
<td>23.3</td>
<td>23.3</td>
<td>23.3</td>
</tr>
<tr>
<td>InSb</td>
<td>$^{115}\text{In}^+$</td>
<td>64</td>
<td>14.4</td>
<td>66</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
</tr>
</tbody>
</table>

$^a$ The accuracy of the evaluation of average energies is of about $\pm 1$ eV, the uncertainty of $I_{\text{scal}}$ is less than 2%. The values of $E_{\text{avr}}$ and $I_{\text{scal}}$ for the ED of $^{69}\text{Ga}^+$ resulting from 4 keV Kr$^+$ bombardment of GaAs sample are 55 eV and $33.2 \times 10^3$ cps correspondingly.
cannot be fitted by Eq. (5). The quality of the fitting, particularly in the high-energy range, improves with increasing the mass of the second component of the compounds.

5. Summary

The emission energy spectra of Ga\(^+\) and In\(^+\) secondary ions sputtered from different A\(^{III}\)B\(^{V}\) compound semiconductors under steady-state conditions were investigated for the case of 4 keV Ne\(^+\), Ar\(^+\) and Kr\(^+\) bombardment. The data were collected experimentally and by computer simulations in a wide energy range, from 2 to 1000 eV.

It was shown that the EDs are complex, with evident high-energy hump, and cannot be described by the Sigmund–Thompson formula. The measured spectra of Ga\(^+\) and In\(^+\) were adequately approximated by a combination of two model analytical distributions that describe the isotropic linear collision cascades and the primary knock-on atoms (i.e. sputtered atoms that are knocked by fast primary ions and undergo a few soft collisions before ejection only). The relative contribution of these recoil atoms enhances with increasing the mass of the second component (P, As, Sb) of the compounds and as a result higher average energies were measured (e.g. 38, 49 and 87 eV for Ga\(^+\) secondary ions sputtered by 4 keV Ne\(^+\) from GaP, GaAs and GaSb targets correspondingly). Computer simulations by using the MARLOWE sputter code helped to identify the high-energy recoils and to elucidate their formation.

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References

[33] A. Tolstogouzov, unpublished data.