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MARISS study on ion yields of Ne^+ scattered from III–V compound semiconductors

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Abstract

Experiments are reported on the ion yields versus the incident energy (0.6–1.6 keV) of Ne^+ scattered at 120° from Ga and In atoms on the surface of III–V semiconductors (GaP, GaAs, InP, InAs). The measurements were performed using mass-resolved ion-scattering spectrometry. The energy dependencies of Ne^+ on Ga(In) for the compounds were found very similar to those measured for pure gallium and indium samples, without any oscillatory structures in the energy range examined. Elemental sensitivity factors did not depend on the chemical environment ("no matrix effect"). The steady-state surface density of Ga atoms was estimated to be constant for both Ga compounds when the ion-beam energy changed. Similar values of the atomic density were derived for indium in the In-based compounds, but In content in the InAs exhibited a little increase at the bombarding energy below 0.8–1 keV. It was shown that for the III–V compounds, the accuracy of quantification with calibration using only Ga(In) pure standard samples depends on the assumed surface atomic density, which can be modified by the sputter-induced roughness and disordering.
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1. Introduction

After the usefulness of low-energy ion scattering (LEIS) for surface analysis was demonstrated by Smith in 1967 [1], a great deal of work has been done, and LEIS has proved to be an extremely surface sensitive tool allowing quantification of experimental spectra [2–5]. The recorded signal I of primary ions, which are elastically scattered from atoms of the i-component on a surface, is factorised as

$$I_i = I_0 \cdot P_i^+ \cdot \frac{d\sigma_i}{d\Omega} \cdot \Delta\Omega \cdot T_i \cdot R_i \cdot N_i, \qquad (1)$$

where I_0 is the ion-beam current to the sample area "seen" by the detector, P^+ is the ion-survival probability, i.e. the probability that a projectile will escape the surface in an ionised state (as a rule, only singly positively charged ions are considered), $(d\sigma)/(d\Omega)$ is the differential scattering cross-section, $\Delta\Omega$ is the analyser's solid acceptance angle, T is an apparatus coefficient that accounts for the analyser transmission and the detector efficiency, R

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is a factor considering surface roughness and related shadowing ($R = 1$ for a flat surface), and N is the surface atomic density. The product NR is often called "the surface density of visible atoms".

It is conventional to include the ion-survival probability and the differential scattering cross-section into the elemental sensitivity or the scattered ion yield Y, which can be determined by calibration with respect to standard reference materials. The calibration method is only valid if the elemental sensitivity is independent of the atomic concentration in a given matrix and exhibits invariability in different matrices ("no matrix effect").

Neutralization of the scattered ions is a process, which above all may be affected by the "matrix effect". However, no difference in the ion-survival probability was found for He^+ ions scattered from Al atoms in pure aluminium and in alumina [6], as well as, from Si atoms in various compounds [7]. Experiments on metal alloys [8–10] indicated no "matrix effect" too. Whereas this is a general trend in LEIS, a number of exceptions are known [11].

Significant attention was focused on the quantitative LEIS of metal alloys and oxides (see the references above). At the same time, few investigations concern III–V compound semiconductors. Using 2.5 keV Ne^+ projectiles scattered at 90°, Croset et al. [12] demonstrated that the ion yields of any of III(Ga, In) and V(P, As, Sb) elements are insensitive to the "matrix effect". It was found that steady-state sputtering does not change surface composition of GaP, GaSb, InP, InAs and InSb samples considerably. Only in the case of GaAs some surface arsenic depletion was revealed. On the contrary, Armour et al. [13] showed that the GaAs(0 0 1) surface becomes arsenic-enriched under 5 keV Ne^+ and Ar^+ bombardment. Both research were performed with a fixed incident energy of projectiles, E_0. While the dependence $Y(E_0)$ can be a reliable test for the "matrix effect" in LEIS [9], we are unaware of such research for III–V compounds with Ne^+ or other heavy noble gas ions.

Rusch and Erickson [14] reported that the ion yields of He^+ on Ga(In) display distinctive oscillatory features at $E_0 = 0.2$–2.5 keV both for pure elements and for their compounds including the III–V semiconductors. Moreover, these features were found to be "matrix-dependent". It was suggested to employ this effect to extract chemical information about certain elements on the surface, but this was not actually done. No experimental evidence of the oscillatory ion yield behaviour in the energy range 0.4–2.2 keV, neither for Ne^+/Ga nor for Ne^+/In, was observed for the pure Ga and In samples in our recent research [15].

The present study deals with mass-separated energy distributions of Ne^+ ions scattered at 120° from GaP, GaAs, InP and InAs semiconductors. We report on results of the ion yield measurements of metal components (Ga, In) for the incident energy $E_0 = 0.6$–1.6 keV and discuss calibration of the compounds with respect to pure Ga and In reference samples.

2. Experimental

The sample probed were single-crystalline (1 0 0) semiconductor wafers fabricated in the Institute for Physics of Microstructures Russian Academy of Sciences (N. Novgorod). These wafers are conducting at the room temperature due to small impurity doping (10^{16}–10^{18} cm^{-3}). For standard references, ultra-high purity (99.9999%) gallium and indium samples were used [15].

The mass and atomic densities of the samples are listed in Table 1. The bulk atomic density, ρ_a, was derived from the mass density [15]. We suggest that the average surface atomic density, N, and the bulk atomic density are related by $N = \sqrt[3]{\rho_a^2}$. Such approach implies an average density without any crystal-face dependencies [16]. However, when the number of density of the outermost atomic planes is rigorously derived from the lattice distance a, it is found to be similar to that presented in Table 1. For the GaAs(1 0 0) one can calculate $N_{Ga} = 0.638 \times 10^{15}$ cm^{-3} ($a = 0.56$ nm), and our estimate gives 0.625×10^{15} cm^{-3}.

It has been shown [17–19] that the usefulness of LEIS can be considerably enhanced by mass separation of scattered ions. In [18], Wittmaack has denoted this technique as mass-resolved ion scattering spectrometry (MARISS). We use MARISS in our experiments. Details on our system and MARISS measurements have been reported in our

Table 1
Mass and atomic densities of the III–V compounds and pure references (Ga, In)

	Ga	GaP	GaAs	In	InP	InAs
Atomic (molecular) weight (amu)	69.7	100.7	144.6	114.9	145.9	189.8
Mass density (g/cm^3)	5.90	4.14	5.32	7.31	4.81	5.68
Bulk atomic density ($\times 10^{22}$, at/cm^3)	5.09	4.94	4.42	3.84	3.96	3.59
Surface atomic density ($\times 10^{15}$, at/cm^2)	1.37	1.35	1.25	1.14	1.16	1.09

To calculate the number of bulk or surface atomic density of each component of the compound, the corresponding data should be halved.

previous publications [15,19–21]. In brief, a monoenergetic Ne^+ beam (without mass-separation) was produced by an electron-impact ionisation gas ion source IQE 12/38. The incident ions were directed at a fixed incident angle $\psi = 30°$ with respect to the sample surface. The ions backscattered at the angle $\theta = 120°$ were mass and energy analysed by the Hiden EQS 1000. All measurements were fulfilled using the "in-plane" geometry in a small solid angle ($\Delta\Omega \sim 10^{-4}$ sr) under the steady-state bombarding conditions, when the scattered ion intensities are stabilized. This is attained at the primary-ion dose above 10^{16} cm^{-2}. Such a dose is usually enough for surface amorphisation of III–V compounds [22]. The surface purity was monitored with positive and negative secondary ion mass spectra, and the partial gas pressures in the analytical chamber were controlled through the residual gas analysis using the same Hiden EQS 1000 Analyser.

3. Results and discussion

Fig. 1(a–c) shows the MARISS spectra of pure Ga and Ga-based compounds measured in the high (1560 eV), middle (970 eV) and low (590 eV) ion energy regime. The ion intensity is normalized to the ion-beam current. Similar results for pure In and In-based compounds are displayed in Fig. 2(a–c). The spectra measured at the intermediate energies have been omitted in the panels. No correction such as background subtraction, smoothing, etc. has been applied to the spectra. The relative peak energies are almost independent on E_0, and their numbers agree with those calculated

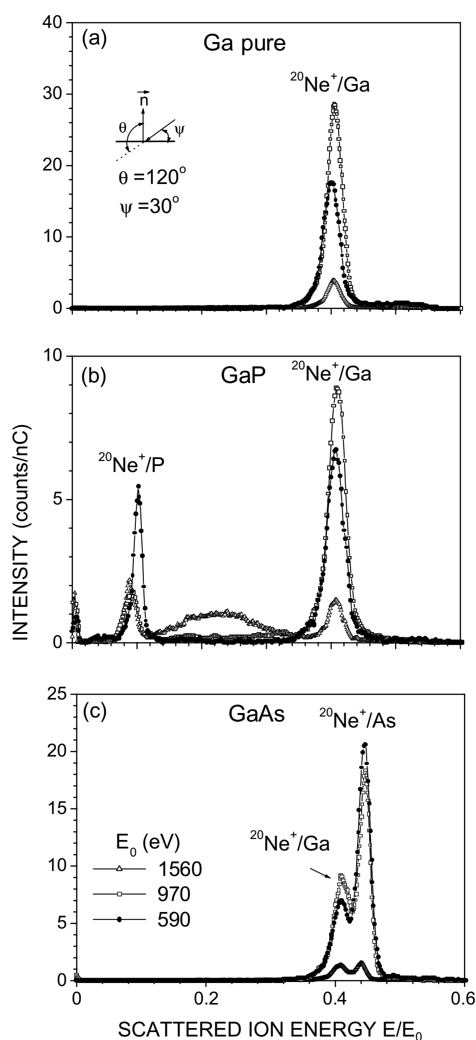

Fig. 1. Mass-resolved energy distributions of $^{20}Ne^+$ ions scattered from pure Ga (a), GaP (b) and GaAs (c) samples at different incident energies.

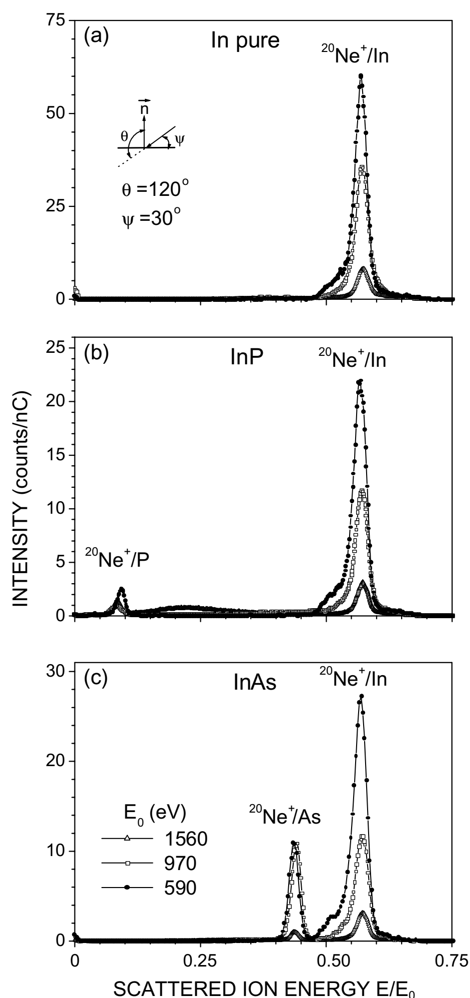

Fig. 2. Mass-resolved energy distributions of $^{20}Ne^+$ ions scattered from pure In (a), InP (b) and InAs (c) samples at different incident energies.

via the binary elastic collision model. Some deviations from the calculated values, mainly for Ne^+ scattered from phosphorus atoms, may be due to the uncertainties in the E_0 and θ measurements and (or) due to inelastic energy losses [19,23], which are rather typical for surface atoms with masses close to the projectile's mass. The GaP and InP spectra recorded at $E_0 = 1560$ eV (Figs. 1(b) and 2(b), respectively) contain the background mound with a maximum located near (0.2–0.25) E/E_0. Such a mound is usually attributed to re-ionised particles scattered from the atoms in deeper layers after single or multiple collision events [2,24]. Another interesting feature of the GaP spectrum is a presence of the narrow peak near zero energy. This peak is caused by Ne^+ ions initially implanted and then re-emitted [17,19].

The effect of the primary ion energy on the scattered peak intensity is shown in Fig. 3(a–b). Peak intensities are estimated via the peak heights normalized to the ion-beam currents. No oscillatory structures, which manifest themselves in He^+/Ga(In) yields of the III–V compounds [14], are found for Ne^+ projectiles in our study because the distance of closest approach between colliding particles under the given experimental conditions are too large for such oscillations to occur [15].

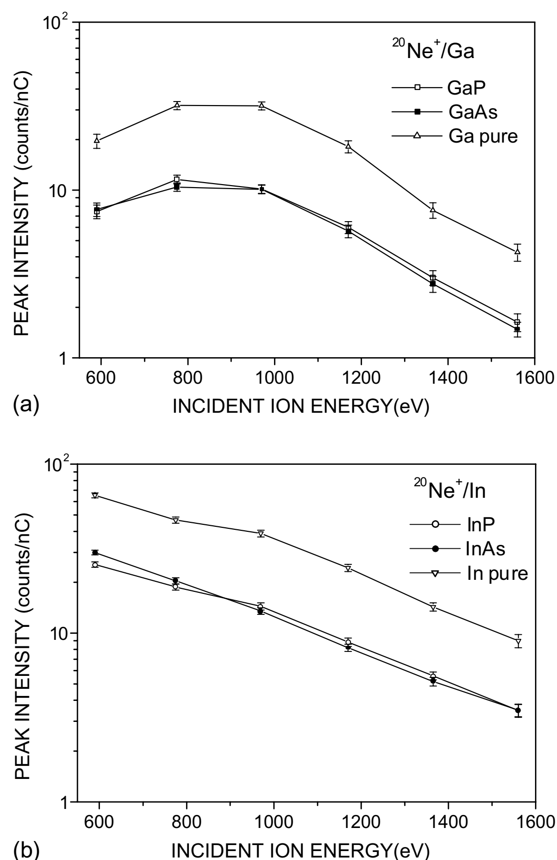

Fig. 3. Peak intensity of $^{20}Ne^+$ ions scattered from Ga (a) and In (b) atoms in the reference samples and III–V compounds at different incident energies.

The energy dependencies of Ne^+ on Ga (Ne^+ on In) exhibit the same shape for the pure reference samples and for the compounds, and the curves of both Ga-based (In-based) compounds look very similar. This shows that the "matrix effect" is not present in our measurements. Additional confirmation can be found in Fig. 4, which shows how the relative elemental sensitivity $Y^+_{\mathrm{In}}/Y^+_{\mathrm{Ga}}$ depends on the incident ion energy for pure Ga and In, and for their phosphide (GaP, InP) and arsenide (GaAs, InAs) compounds. We use the relative sensitivity factor, since we do not know the apparatus coefficients T_i (see Eq. (1)). However, we are aware of their independence on the scattered ion energy [21], i.e. $T_{\mathrm{In}} = T_{\mathrm{Ga}}$. The peak intensities are corrected to account for the difference in the initial surface atomic density ("geometrical packing") of Ga- and In-based compounds (see Table 1), which were estimated as N_i/N_j, namely 1.20 (Ga/In), 1.16 (GaP/InP) and 1.15 (GaAs/InAs). In the literature, the relative sensitivity of 1.75 ± 0.06 for 6.7 keV Ne^+ scattered at 137° from the pure In and Ga samples was reported [25].

The curves presented in Fig. 4 almost coincide, i.e. different chemical environment ("matrix effect") has no influence on the scattering ion yields. Only for $E_0 < 0.8$–1 keV, the arsenide curve tends to be a little higher than other ones. Presumably, this means that the surface density of the "visible"

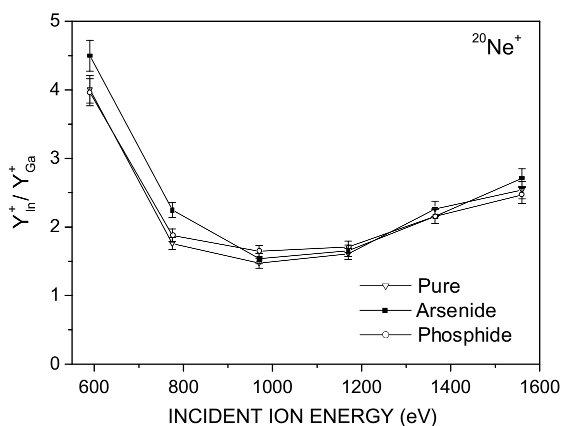

Fig. 4. Relative ion yield as a function of the incident energy for $^{20}Ne^+$ scattered from In and Ga atoms in pure reference samples, phosphide (InP, GaP) and arsenide (InAs, GaAs) compounds.

In atoms in the InAs is different from the simple geometrical packing considered above due to the sputter-induced roughness and disordering effect, which should be more pronounced for InAs than for GaAs [22].

If there is no "matrix effect", one finds from Eq. (1) that surface atomic densities of the reference sample N_i^{ref} and of the considered sample N_i should obey the proportion

$$N_i = \frac{I_i}{I_i^{\mathrm{ref}}} N_i^{\mathrm{ref}} = 100\mathrm{at.\%} \frac{I_i}{I_i^{\mathrm{ref}}} k, \qquad (2)$$

where k is a factor accounting for the difference in the initial surface atomic densities of the reference sample and of the compound.

Using Eq. (2), we estimate the steady-state surface concentration of gallium to be 40 ± 5 at.% in both Ga-based compounds (the error represents only statistical variation between five measurements of peak intensities). A similar value is obtained for indium in the In-based compounds, whereas the indium content in the InAs is higher (48 ± 5 at.%) at the bombarding energy below 0.8 keV. For all samples considered, the Ga(In) surface concentration is not sensitive to the surface-binding energies and atomic masses of the compounds, although it is not stoichiometric either. We are not inclined to attribute this discrepancy to the surface enrichment by another component (P, As) due to preferential sputtering of Ga(In) [22,26,27]. It is more likely that an uncertainty in the k-factor affects accuracy of the quantification procedure, since our estimation of the surface atomic densities is based on the ideal geometrical packing. Real surfaces are disordered by ion bombardment, and sputter-induced roughness may be different for the reference samples and the investigated ones. It is generally acknowledged that accurate estimation of the surface density of "visible" atoms, which are involved in scattering events, is an issue and the related uncertainty can reach a factor of two [9,28].

To some extent, direct measurements of P and As reference samples can make this problem more tractable. Calibration against two standards was successfully applied to binary metal alloys (for a review see e.g. [10]). However, investigation of pure phosphorus and arsenic references under

UHV conditions is very difficult, and at this stage we have restricted our study to calibration with respect to pure Ga and In reference samples.

4. Summary

Ion yields of Ne projectiles scattered from Ga and In atoms on the surface of III–V compound semiconductors (GaP, GaAs, InP, InAs) were measured within the incident energy range 0.6–1.6 keV by mass-resolved ion-scattering spectrometry. The main results are summarized as follows:

(1) The energy dependencies of Ne^+ on Ga(In) for the III–V compounds were found to be very similar to those measured for pure gallium and indium reference samples, without any oscillatory structures in the energy range examined.
(2) The ion yields (elemental sensitivity factors) were independent of the chemical environment, i.e. "matrix effect", which is able to complicate quantification in III–V compounds, was not revealed.
(3) The steady-state surface density of Ga atoms was found to be the same for both Ga-based compounds, and its value (40 ± 5 at.%) was independent of the ion-beam energy. Similar value of the surface atomic density was estimated for indium in the In-based compounds, but In content in the InAs exhibited a little increase (48 ± 5 at.%) at the bombarding energy below 0.8–1 keV. Conceivably, sputter-induced roughness and disorder were responsible for such effect. It was shown that the accuracy of quantification in III–V compounds with calibration using Ga(In) pure standard samples depends on the assumed surface atomic density, and uncertainties in its value can cause a significant slip in the concentration scale (up to 20% in our measurements).

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