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An upgraded TOF-SIMS VG Ionex IX23LS: Study on the negative secondary ion emission of III–V compound semiconductors with prior neutral cesium deposition

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ABSTRACT

A TOF-SIMS VG Ionex IX23LS with upgraded data acquisition and control system was used to study the secondary emission of negative atomic and cluster ions of non-metallic elements (P, As and Sb) upon a 19 keV Ga^+ bombardment of non-degenerated III–V semiconductors (GaP, GaAs, GaSb, InP, InAs and InSb) with prior neutral Cs deposition from a getter dispenser. It was found that surface cesiation enhances the peak intensity of all negative ion species; in the case of atomic ions, the greatest increase (360) was observed for P^- emitted from InP. Such an enhancement was larger for In-based than for Ga-based compounds. We explained that in terms of an electronegativity difference between the composing atoms of III–V semiconductors. The greater electronegativity difference (bond ionicity) of In-based compounds resulted in the greater Cs-induced work function decrease leading to a higher increase in the ionization probability of secondary ions.

1. Introduction

Secondary ion mass spectrometry (SIMS) is a mature surface analytical technique with a vast range of application in materials science, microelectronics, biology, medicine, geoscience, etc. [1]. In the past two decades, advances in SIMS application have stimulated the development of novel instrumentation with time-of-flight or magnetic sector mass analyzers. However, such state-of-the-art SIMS equipment is very expensive, making it affordable for a limited number of university laboratories and research centers. Simultaneously, the development of "low-cost" MiniSIMS by Millbrook [2] proved unsuccessful due to the poor analytical characteristics of this machine. Custom-built installations based on commercially available mass analyzers and ion-beam sources along with bolt-on SIMS are reasonably priced instruments as against standard SIMS; quite a few quality applied and fundamental investigations have been carried out using these (see, for example, [3,4]). An alternative approach consists in upgrading the SIMS equipped with old-fashioned data acquisition and control system, but possessing both vacuum and analytical facilities of acceptable quality.

In this work, we describe the results of the upgrade of an IX23LS TOF-SIMS, developed and manufactured by VG Ionex (Burgess Hill, UK) in the mid-eighties [5,6], and report on its recent application for the study on negative secondary ion yields of III–V semiconductors with neutral cesium deposition onto the sample's surface before SIMS analysis.

It has long been known (see, e.g. [7–9] and references cited therein) that deposition and shallow implantation of alkali metals, especially Cs, stimulates negative secondary ion emission from metals and semiconductors due to the decrease of their electron work functions. Along with Cs^+ ion-beam bombardment, routinely used for that in standard SIMS, neutral cesium deposition prior to or during SIMS analysis has proved to be a useful tool allowing the separation of cesium incorporation and cesium ion-beam sputtering [10]. Great attention was given to pure metals and elemental semiconductors including thin film structures [10–12] (to name but a few works). A lack of systematic data concerning III–V compound semiconductors has motivated us to study the manner in which Cs^0 deposition influences the secondary emission of negative atomic and cluster ions of non-metallic elements (P, As and Sb) upon Ga^+ bombardment of Ga-based and In-based binary semiconductors. The applications of our instrument for materials and thin films characterization and also for the identification of human calculi have been discussed elsewhere [13–15].

2. The instrument

2.1. General description

The schematic diagram of an upgraded TOF-SIMS VG Ionex IX23LS is shown in Fig. 1 and its main features are briefly

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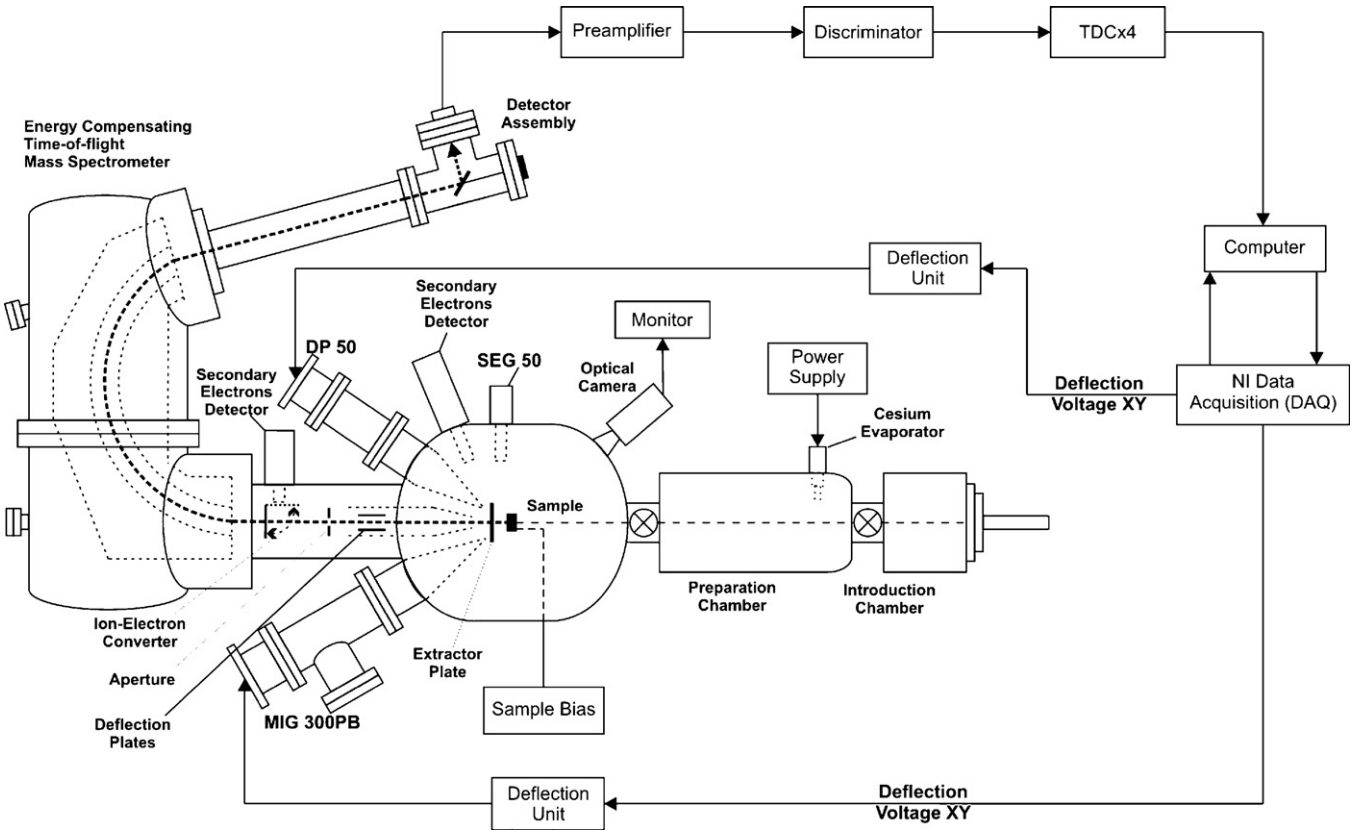

Fig. 1. Schematic view of the upgraded TOF-SIMS VG Ionex IX23LS.

summarized below. The instrument was assembled as a fully bakeable ultra-high vacuum (UHV) system composed of three stainless steel vessels isolated from each other by UHV gate valves and evacuated using Edwards EO4 diffusion pumps with polyphenyl ether pumping fluid and incorporating CCT100 liquid nitrogen cold traps. Throughout the course of the experiments the pressure in the analytical chamber is maintained at the level of $(0.5–1) \times 10^{-7}$ Pa. The duoplasmatron ion-beam column possesses two differential pumping stages, and the liquid–metal ion gun is equipped with an auxiliary 30 l s^{-1} ion pump to reduce the oxygen pressure in the source's region. The vacuum system did not undergo any major alterations, only a resistance heated evaporator with a replaceable Cs dispenser by SAES Getters (Milan, Italy) was mounted in the preparation chamber.

Positive and negative secondary ions are analyzed and detected using the energy-compensated mass spectrometer consisting of a 164.4° Poschenrieder-type analyzer [16–18] with a flight path of 2.26 m [6] and newly installed Chevron™ MA detector assembly with two microchannel plates by Photonis (Sturbridge, MA, USA). Extraction of the secondary ions is performed along the normal to the sample surface applying ±5 kV to the sample holder; the distance between the sample surface and extraction electrode is situated between 5 and 10 mm. Typical mass resolution is 300 (full width at half maximum) and mass range is 0.5–1000 Da.

A liquid–metal ion gun MIG 300PB is used as a source of analysis ions with an incident angle of 60° to the surface plane (excluding the change of the ion-beam direction due to the accelerating-retarding electric field in the space between the sample surface and extraction electrode). At present, this gun is fitted with a Ga field emitter operating at up to 30 kV. The gun has condenser and focus asymmetric einzel lenses, a Wien mass filter for separation of $^{69}Ga^+$ and $^{71}Ga^+$ isotopes, octupole stigmators and scan rods. For continuous beam with the maximum size aperture a sample current of 30 nA is obtained. In pulsed mode, auxiliary internal deflector plates chopped the ion beam producing 5–50 ns pulses with a maximal repetition frequency of 20 kHz.

We plan to substitute pure gallium for In–Bi alloy with minor modification of the source's construction. For In66.3/Bi33.7 the melting point is ca. 72 °C that is not very above the operating temperature of a standard Ga source. The modified source should produce Bi_n^+ cluster ions improving secondary ion yields of heavy molecular species [19]. We are also going to deploy room temperature ionic liquids [20] – molten salts characterized by melting points below 100 °C – as working matter for the production of the analysis ions, in a similar way as liquid metals and alloys using field ionization. Such a source can operate in bipolar mode producing molecular ions with both positive and negative polarities [21]. Recently, we have performed time-of-flight studies [22,23] on the field evaporation of 1-alkyl-3-methylimidazolium bis(trifluoromethylsufonyl)imide, where alkyl is ethyl, butyl and hexyl, using the scanning atom probe at the Kanazawa Institute of Technology, Japan. Non-degraded cationic ions at m/z 111, 139 and 167 along with positive cluster ions composed of the intact cations and anions' fragments were observed.

SIMS depth profiling is carried out in the dual beam mode [24] using a DP50B duoplasmatron gun by VG (East Grinstead, UK) for the controlled removal of the sample materials. This gun operates with a hollow "cold" Ni cathode producing 1–10 keV O_2^+ ions with the incident angle of 60° to the sample surface. The ion-optical column contains 3 lenses (two condensers and a focus), a Wien mass filter with external magnets and scan quadrupoles. The analysis and sputter ion beams are interlaced in the course of depth profiling. At first, 14–20 keV Ga^+ pulsed beam performs the analysis with ±5 kV potential applied to the sample. Then, during 2–5 s the sample potential is decreased to zero, and then, a 2–8 keV O_2^+ continuous beam of 100–150 nA and 30–50 nm spot erodes the