High Spatial Resolution Surface Analysis Using TOF-SIMS

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Abstract

High performance elemental as well as molecular surface analysis can be realized by time-of-flight (TOF) secondary ion mass spectrometry (SIMS), i.e. the analysis of secondary ions or laser postionized secondary neutrals, which are emitted from a solid surface under primary ion bombardment. The technique allows the detection of all elements, the distinction between isotopes, and the detection of large and even involatile surface molecules. It features a pronounced surface sensitivity, high mass resolution, high absolute sensitivity, high mass range, high lateral resolution and in addition high depth profiling performance, if it is operated in a dual beam mode. TOF-SIMS can be applied to all kinds of materials including insulators like glasses, ceramics or polymers. The technique has been applied successfully to metals, oxides, semiconductors, molecular overlayers, polymers, etc. It is increasingly employed for fundamental and applied research as well as for product development and production control, in a wide variety of fields ranging from chemistry and microelectronics to life sciences and environment control.

1. Introduction

Secondary ion mass spectrometry (SIMS) is a well established and powerful technique for the analysis of solids. The technique is based upon the phenomenon that heavy particle impact on a solid surface results in the emission of secondary ions (SI), originating from the outermost surface layer of this solid. The quality of a SIMS analysis depends strongly on the type of mass spectrometer applied for the mass analysis of the corresponding secondary ions [1].

SIMS started originally with single and double focusing magnetic sector field instruments, applied mostly in the dynamic mode for element analysis. This dynamic mode is characterized by high erosion rates up to hundreds or thousands of monolayers sputtered during a single analysis. Sector field SIMS has been applied very successfully in the semiconductor industry as a standard technique for high sensitivity depth profiling of dopents in silicon, e.g.

A further step in the development of SIMS was its application to surface characterization. Here mostly quadrupol instruments were used because of their compact size, high registration speed and relatively high transmission. By an extreme reduction of the erosion rate (static SIMS), the uppermost monolayer of a solid became available for a SIMS analysis. Static SIMS has been widely applied to the analysis of molecular surfaces, the investigation of molecular surface reactions, etc. [2]. In combination with electron beam postionization quadrupole SIMS allows the analysis of sputtered neutrals. Quadrupole SIMS is applied very successfully in the dynamic mode where it competes with magnetic sector field instruments in high sensitivity depth profiling [3].

Originally time-of-flight mass analysers have been introduced for static SIMS investigations [4]. For this operation mode the time-of-flight principle features some unique advantages, in particular if the amount of sample material available for the analysis is very limited, as in monolayer, small particle, and interface analysis. The unique combination of high mass resolution, high transmission, unlimited mass range, and quasiparallel mass registration makes TOF-SIMS a most powerful technique for surface, interface, and thin film analysis. In combination with a rastered fine focused primary ion beam it allows microarea analysis as well as surface and interface imaging (chemical mapping). The pulsed operation of time-of-flight instruments, allows an ideal combination with pulsed high power UV-lasers for efficient postionization of sputtered neutrals [5].

Today TOF-SIMS in its different operation modes is a widely applied and most powerful technique, with applications ranging from particle identification on Si wafer surfaces to the analysis of plasma modified polymer surfaces [6,7].

2. Basic Process

The fundamental process, SIMS is based upon, is the impact of a single heavy particle - for many reasons it is in general an ion - on a surface (Fig. 1). This primary ion (PI) penetrates into the solid, transferring its energy to surface near target atoms. By further impact processes these atoms generate a local impact cascade and a fraction of the deposited PI energy will be transferred back to the surface with an outwards direction of momentum. If the energy transfer to a surface particle is exceeding its binding energy to the surface, this particle will be separated and will be emitted.

This basic process can be characterized by a number of figures : The sputter yield Y describes the average number of surface particles - e.g. atoms - removed from the surface by one single PI impact. The damage cross section σ describes the depleted surface area (Fig. 1). The sputtered particles may be neutrals or they may be positively or negatively charged. The SI yield Y_i^q describes the average number of ions X_i^q, in charge state q, generated by a single PI impact.

Y, σ and X_i^q are quite different for different solid surfaces (metals, semiconductors, alloys, molecular overlayers, polymers, etc). In addition they depend to a certain degree on the energy and the mass of the bombarding primary particle. For metal surfaces bombarded by keV noble gas ions, sputter yields are in the range of 10 atoms/primary ion, corresponding to a damage (depletion) cross section in the range of some 10^{-13} cm^2. Positive metal ion yields Y^+ range between 10^{-2} and 10^{-6}. From more complex samples - e.g. molecular overlayers - a variety of secondary particles Y_i^q, neutrals as well as ions, are emitted. This holds for example for polymers. Here sputter yields range between 10 and 1000, corresponding to damage cross sections between 10^{-13} and 10^{-11} cm^2.

Many different processes may be responsible for the ionization of sputtered particles, as bond breaking, protonation or deprotonation, electron loss or attachment, etc.

3. Time-of-Flight SIMS

Sputtered particles are emitted with relatively low kinetic energies in the range of some eV only. In a time-of-flight instrument these ions are accellerated to an energy of some keV. Then their velocity depends on their q/m ratio. The determination of the corresponding flight time allows the determination of q/m and m.

Fig. 2 shows the scheme of a modular TOF-SIMS instrument. SI generation occurs by a pulsed, mass separated and focused primary ion beam (1). The accellerated secondary ions travel along an energy focusing drift path (2). They are detected by a single ion counting detector (3) with a time resolution at least comparable with the primary ion pulse length. For each detected secondary ion the flight time and - in the case of surface imaging with a rastered focused ion beam - its origin (x, y, z) on the surface is storaged. An additional secondary electron detector close to the sample

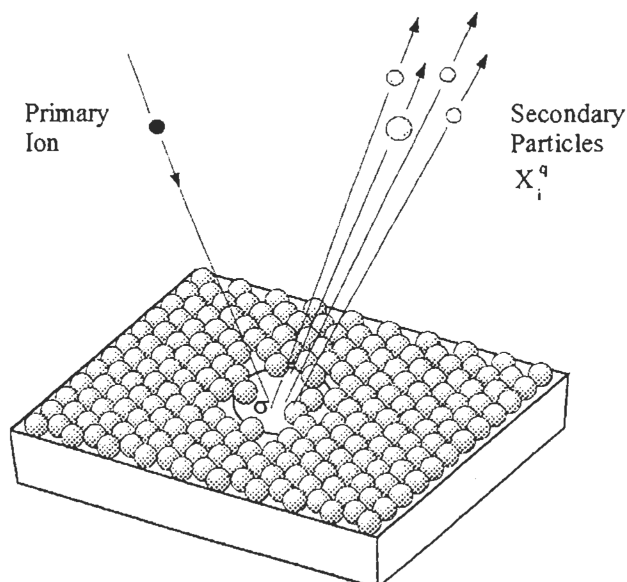

Fig. 1 Surface sputtering results in the emission of a variety of secondary particles X_i^q in different charge states q

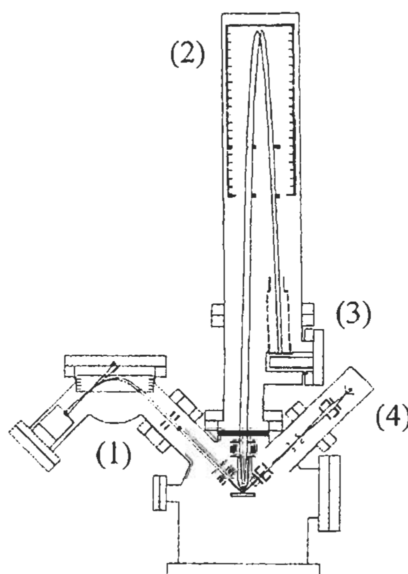

Fig. 2 Scheme of a modular TOF-SIMS instrument

allows the detection of ion induced secondary electrons (SE). The registration of SE images requires only a very low primary ion fluence. This results in a correspondingly reduced surface damaging.
The pulsed secondary ion generation allows pulsing of the extraction field and the injection of low energy electrons (4) between two successive primary ion pulses. This enables a perfect charge compensation in the case of insulating samples.

4. TOF-SIMS Operation Modes

TOF-SIMS allows three main operation modes : Surface spectroscopy, surface imaging, and depth profiling.
In the spectroscopy mode a rather large surface area (typically > 100 μm^2) is bombarded under static SIMS conditions. The large area allows high sensitivity surface analysis and is applied e.g. for element trace analysis in the uppermost monolayer of a solid, the identification of molecular surface species, the investigation of surface reactions, molecular overlayers, thermal desorption and diffusion processes on surfaces, etc. [6,7]. Fig. 3 shows as an example the positive SI spectrum of a polystyrene monolayer on Ag [6] obtained by static SIMS.
In the imaging mode a fine focused primary ion beam is rastered over a surface area typically between 5×5 and 500×500 μm^2. For each pixel the complete spectrum is storaged. This allows the reconstruction of images for any combination of peaks, from any part of the imaged area. In this imaging mode static as well as dynamic SIMS operation is possible. The reconstructed Cl^- and $AgCl_2^-$ images of AgCl single crystals are presented in Fig. 4. Data acquisition required the consumption of about one monolayer.
Depth profiling requires high primary ion fluences which cannot be delivered by the pulsed PI beam. In the dual beam mode high fluences are supplied by an additional sputtering beam which is generated by an independent additional sputter ion source. This source generates low energy ion pulses, reaching the surface between each two primary ion pulses of the analytical PI beam. This combination allows multicomponent depth profiling up to the µm-range with ultimate depth resolution and sensitivity. Fig. 5 presents a multielelement depth profile of a 600 nm AlGaAs multilayer. For ultimate depth

Fig. 3 Positive static SIMS spectrum of a monomolecular polystyrene overlayer on Ag [2]

Fig. 4 Reconstructed Cl^- and $AgCl_2^-$ secondary ion images of AgCl crystallites [8]

Fig. 5 Multielement depth profiling of an AlGaAs multilayer by dual beam TOF-SIMS [9]

resolution molecular sputtering by 1 keV SF_5^+ ions has been applied [9].

By combining the depth profiling with the imaging mode, 3D analysis becomes feasible, provided for each detected secondary ion the x,y,z-coordinates of its local origin are storaged. Then spectra and images of any part of the analyzed volume and any peak or peak combination can be reconstructed.

Spectroscopy and imaging as well as depth profiling can be realized for positive or negative secondary ions, and in addition for postionized sputtered neutrals. These neutrals are postionized most efficiently by an appropriate interaction with a laser beam. Quite a number of different ionization schemes as resonant postionization, nonresonant multiphoton or nonresonant single photon ionization have been applied. For element analysis nonresonant multi photon ionization (NRMPI) is the most efficient way for postionization. Laser-SNMS is applied in combination with all three operation modes, surface spectroscopy as well as imaging and depth profiling [10].

5. Future Developments

Originally designed mainly for the detection of large involatile organic molecules by static SIMS and for the analyis of the uppermost monolayer of a solid, TOF-SIMS has developed into a most powerful technique for microarea analysis, imaging (chemical mapping), and most recently for depth profiling with ultimate depth resolution. The integration of large sample stages (8“ wafers), focused ion beams (FIB) for sample machining, heating and cooling devices, and the development of sophisticated software, results in an increasing application of this technique in a variety of different fields as microelectronics, chemistry, life sciences, etc.

Future development will focus on a number of issues. A most important one is fundamental research, i.e. the secondary ion formation process itself as well as the application of static SIMS in surface science. A second important development concerns the use of laser postionized sputtered neutrals, for element analysis as well as for the detection of surface molecules in biological samples, e.g. Another direction will be the integration of and the combination with other excitation sources, and the more sophisticated use of all emitted secondaries (ions, neutrals, electrons, photons). Besides the instrumental developments, the generation of libraries, in particular for the identification of molecular surface species, will become increasingly important.

Even with its present performance, without any further instrumental and methodological developments, there exists already a large analytical potential of TOF-SIMS. This includes completely new fields where e.g. molecular surface information is required, as well as many traditional fields of surface analysis where the required combination of element range, sensitivity, lateral resolution and depth resolution may not be achieved by standard techniques like AES, XPS, EMP or TEM.

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