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MCs_n^+ -SIMS: an innovative approach for direct compositional analysis of materials without standards

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Abstract

This review primarily deals with the compensation of ‘matrix effect’ in secondary ion mass spectrometry (SIMS) for direct quantitative analysis of materials using MCs_n^-SIMS approach. Emphasis has been given on exploring the formation mechanisms of MCs_n^- (n = 1, 2,..) molecular ions (M denotes the element to be analyzed and Cs^- is the bombarding ion) emitted in the SIMS process. Following a brief introduction on SIMS, a study on MCs_n^- molecular ions emitted from various metal targets under Cs^- primary bombardment has been discussed. These studies essentially concentrate on the secondary ion energy distributions of the emitted species under different bombarding energies and impact angles. We have discussed a systematic study on the effect of reactive species like oxygen and cesium on the emission of MCs_n^+ molecular ions. In all cases we have estimated the changes in local surface work function from the leading parts of the secondary ion energy distributions. The observations are explained in the light of surface work function changes at the sputtering sites. Formation mechanisms of MCs_n^- molecular ions are explained in the framework of sputter-ion emission models. Suppression of matrix effects in the compositional analysis of molecular beam epitaxy (MBE) - grown SiGe alloy structures has been discussed in detail. We have essentially applied the MCs^-SIMS method for the minimization of ‘matrix effect’, which is routinely encountered in conventional SIMS analysis hindering quantification of materials. Under the impact of energetic Cs^- ions, both SiCs^- and GeCs^- ions have been monitored for SiGe alloy samples with Ge concentration between 0 and 72 at.%. Following optimization of various experimental parameters, we have shown that the matrix effects are practically suppressed for Ge content up to 72 at.% in SiGe samples. A procedure for the accurate quantification of Ge concentration in Si_{1-x}Ge_x alloys using this method has been presented. This novel methodology has successfully been applied in the depth profiling of Si/Ge multilayer structures grown by MBE technique.

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1. Introduction

The rapidly growing importance of advanced materials stems from the ever-increasing importance of thin films. For example, some fast developing areas are: thin film structures for microelectronics with tailored electrical properties, optical films with specific anti-reflecting and transparent properties, coatings and beam modified surfaces with high resistance to wear and corrosion etc. Controlled fabrication of these films requires a detailed and reliable, spatially-resolved chemical and structural analysis. In view of their planar structure, the analysis of in-depth distributions of chemical composition with high resolution is of primary importance, particularly near surfaces and interfaces. For this purpose, numerous methods have been developed during past five decades [1, 2]. Among these, micro-sectioning techniques based on sputtering in combination with surface analysis methods are most frequently applied [1-8] because they are applicable to practically any kind of materials and allow the attainment of optimum depth resolution (down to a few atomic monolayers) over a wide depth range up to several micrometers. There are many techniques available for performing an analysis of the elemental, chemical and physical makeup of a material. Many of these techniques are inexpensive to set up and operate, others are easy to interpret and some provide an absolute measurement capability. In short there is a large spectrum of techniques open to someone who wishes to do materials analysis of a sample. Each of these techniques has its own pros and cons and each its own niche. Conventional Ion Beam Analysis (IBA) techniques are far from the cheapest techniques to apply and can be complex to interpret. The scientific world has become more sensitive to costs and employing an expensive technique when a cheaper one would do is not a sustainable option. Consequently, for IBA techniques to continue to be used at the forefront of research they must be seen to be providing something more than can be achieved via other methods. This might be in terms of the quality of the data, the speed of analysis (thereby effectively reducing the cost) or simply the only way to obtain a particular measurement.

Properties of material interfaces on atomic scale govern a great number of material properties and macroscopic phenomena. For example, structure and composition of surfaces (i.e. solid/vacuum interfaces) are responsible for all kinds of interaction of solids with ambient media as observed in adsorption, oxidation, corrosion, catalysis, friction and wear. Material properties such as brittle fracture, creep and re-crystallization are governed by the structure and composition of internal interfaces, for example, grain boundaries. In layered thin-film structures, the mechanical, thermal and chemical stability of interfaces between different materials (hetero-interfaces) is the way to reliable performance of many technological products such as microelectronic devices, sensors, components and protective coatings in various instruments, tools and medical prosthetics technologies. Despite the recent progress in interface science and technology, many details of the correlation between macroscopic physicochemical behaviour and microscopic property/composition/structure relationships of interfaces is not yet sufficiently well understood. The key to the study, control and optimization of interfacial properties appears to be a close link between the preparation and synthesis of interfaces and their chemical and structural characterization.

In particular, interfacial microchemistry is significant for the properties of interfaces [9]. The primary aim of the chemical analysis of interfaces is to determine their elemental composition and that of their surroundings with high spatial resolution, ultimately over atomic dimensions. Among the various techniques developed for this purpose, surface and interface analysis methods in combination with ion sputtering [5, 10-13] are most frequently applied because they are applicable to almost any kind of solid materials and allow the attainment of optimum depth resolution in the atomic monolayer region over a
wide depth range up to several micrometres. In the context of sputter depth profiling, secondary-ion mass spectrometry (SIMS), secondary-neutrals mass spectrometry (SNMS), glow discharge spectroscopy (GDS), Auger electron spectrometry (AES), x-ray photoelectron spectroscopy (XPS), ion scattering spectrometry (ISS) have always found their place among the most important methods for surface and interface analysis [1, 14].

Fig.1. Schematic showing instrumental parts and principal arrangement of a surface analysis instrument for sputter depth-profile analysis.

Today, depth profiling using surface analysis methods in combination with ion sputtering has attained a high degree of maturity. Refinements of instruments and experimental techniques have led to great improvements in depth resolution. Instrumentation for depth profiling requires a source of energetic ions impinging on the sample surface and a suitable means of analysis of either the sputtered material or the residual surface after a certain sputtering time, as schematically depicted in Fig. 1. The ion source is usually an ion gun with beam raster facility, or low-pressure DC or RF plasma from which the ions are extracted. Analysing the sputtered particles (ions in Secondary Ion Mass Spectrometry (SIMS) or neutrals in Secondary Neutral Mass Spectrometry (SNMS)) in a mass analyzer during primary-ion bombardment yields direct information about the sample composition with depth. Alternatively, the optical emission of excited species can be determined by an optical spectrometer: Glow Discharge Optical Emission Spectroscopy (GDOES).

The complementary method is the analysis of the residual surface, for example, by electron or x-ray excitation and measurement of the secondary Auger- or photoelectron spectra with a charged-particle energy analyzer (AES and XPS). The latter can also be used for elemental analysis of the first surface layer by the determination of the primary ion energy loss due to surface scattering, as performed in Ion Scattering Spectroscopy (ISS). The basic procedure of depth profiling consists of recording the element specific peaks detected with the respective analyzer as a function of the sputtering time. For constant ion energy and beam current density the latter is proportional to the sputtered depth if the sputtering rate does not change with time.

Bombardment of a surface with energetic primary particles leads to surface erosion by emission of secondary particles from the sample. By continuous sputtering, layers beneath the original surface are subsequently exposed. *Hence there are two ways to obtain the in-depth distribution of composition as a*
function of the sputtered depth: either by mass spectrometric analysis of the sputtered matter, as in SIMS and SNMS, or by chemical analysis of the remaining surface, as in AES, XPS and ISS in conjunction with sputter erosion of the material [2, 8]. These methods are markedly different with respect to elemental specificity and sensitivity, dynamic range, information depth etc. The sputtering process itself, however, is independent of the analysis method and should therefore be considered as a separate physical process. Sputtering can be accomplished by removing atoms from the top monolayers of a solid [15, 16]. Therefore, a depth resolution in the monolayer regime should in principle be achievable. However, sputtering does not occur by an ideal layer by layer removal but is the result of a complex ion beam - sample interaction process. This process introduces a variety of distortional effects into the original morphology and composition of a sample, which are the cause of the much more extended profile broadening generally observed.

Recent progress in understanding the main physical processes and parameters involved in sputter erosion as well as its implications in specific surface analysis methods has led to a general framework of optimized profiling conditions for the achievement of high depth resolution. Glancing incidence of the ion beam (e.g. 80° to the normal to the sample surface) and low ion energy (< 1 keV) have pushed the depth resolution to its physical limits [6, 13, 17]. For this purpose low-energy (200 eV) ion guns with high current density have recently been developed [18]. Alternatively, molecular ions at higher energy can be applied because on impact the total energy is divided between the different atoms of the dissociating molecule [19], thus achieving a total depth resolution of 1.4 nm. In general, depth resolutions below 2 nm can now routinely be attained. In addition, the deconvolution of depth profiles by an experimentally determined resolution function is increasingly coming into use and enables us to reconstruct the original profiles with a precision of about one atomic monolayer [20-27].

Depth profiling is performed by ion bombardment of a selected area of a sample and subsequent analysis of a smaller area centred within the rastered area to avoid crater edge effects. A prerequisite for a meaningful in-depth analysis is a laterally homogeneous elemental distribution in planes parallel to the surface within the analyzed area. The experimental result consists of an elemental signal intensity as a function of the sputtering time (or the primary ion dose, in case of a calibrated ion beam current density). In general, these raw data represent a more or less distorted image of the original, ‘true’ in-depth distribution of composition. To obtain the latter, three fundamental tasks have to be solved [4-7]: (a) conversion of the sputtering time into depth, (b) conversion of the signal intensity from the surface compositional analysis method into concentration, and (c) assessment and correction of the shape distortions of a sputter profile, particularly near steep concentration gradients. These distortions limit the precision of a measured profile as described by the resolved depth, which is commonly identified as depth resolution \( \Delta z \). These three problems are closely interlinked and can only be considered separately in a first order approximation.

2. Secondary Ion Mass Spectrometry

The fundamentals in Secondary ion mass spectrometry (SIMS) were laid by Herzog and Vihboeck (1949) [28]. Honig (1958) [29] constructed the first complete secondary ion mass spectrometer capable of sputter depth profiling. The first commercial SIMS for micro-analytical applications was introduced by Liebl (1967) [30]. Applications to semiconductor and thin-film analysis were shown by Werner (1968) [31] and depth profiling of thin surface layers was successfully demonstrated by Benninghoven (1969) [32] by the development of the ‘static’ SIMS method.
Figure 2 shows the schematic representations of the technique. In this technique, the primary beam removes atomic layers of the sample at a rate determined by the intensity, mass and energy of the bombarding ions and by the physical and chemical characteristics of the sample itself. SIMS has evolved towards a cornerstone in many materials studies within the semiconductor community due to its excellent sensitivity, quantification accuracy and depth resolution. In recent years its application has expanded from simple, relatively deep dopant profiling in a single matrix towards the analysis of very shallow (<10 nm) profiles contained in complex structures and buried below (ultrathin) metallic films (which are used as gate or silicide material). These changes have increased the demand for SIMS with very high depth resolution considerably [33]. Moreover SIMS starts to be used to study the material interactions within these structures. Whereas the original quantitative success of SIMS was based on its use within the dilute limit i.e. the analysis of a minor (low level) constituent in a single matrix, the present applications have evolved towards the analysis of very high concentration levels and matrix compositions, thereby violating the basic assumptions put forward originally to quantify SIMS results accurately. Evidently, changes in ionization probabilities and sputter yields occur when going from one matrix to another one, thereby requiring complex data treatments and calibration procedures [34, 35]. Based on these observations it is clear that one needs to consider all the fundamental SIMS mechanisms contributing to the quantification, depth scale errors and depth resolution. The mechanisms underlying the potential errors can be identified by realizing that in addition to the desired process (i.e. the mass analysis of a sputtered, partially ionized, particle flux which can be converted into an intensity profile) concurrent processes occur. Indeed the energy deposition by the primary ion leads to the development of a collision cascade which induces not only the sputter process but also causes at the same time many atomic displacements and thus a modification of the (instantaneous) internal profile.

Although the collision cascade is determined by the primary ion-matrix combination, the obtainable depth resolution for different elements is element specific [36]. This can be rationalized by considering the important mechanisms involved:

(1) The extent of the collision which determines the depth over which layers are intermixed. Obviously a larger mixing depth will mean a larger decay length. This mixing depth will scale with the primary ion energy (and penetration depth) leading to the universally observed scaling of the decay length with energy. (2) The amount of energy deposited within the collision cascade. Indeed when comparing similar penetration depths for different primary ions, these can only be achieved with higher/lower energy
for the heavier/lighter ion. Hence, the energy deposition density and thus the number of displacements induced will be different. As long as the mixing has not yet led to a completely homogenized mixed layer, more displacements will imply longer decay lengths. (3) The energy transfer between a recoiling matrix element and the impurity and the distance traveled by this element for a given energy transfer. Both effects are element specific and cause the observed differences in decay lengths.

(3) **Matrix Effect in Secondary Ion Mass Spectrometry**

Secondary emission of ions in the sputtering process is an inelastic phenomenon in ion surface interactions and has tremendous important applications in materials analysis. In SIMS [37], the ionized fraction of the sputtered species (known as secondary ions) is detected by a mass spectrometer equipped with appropriate ion collection optics. SIMS is sensitive to all elements in the periodic table, including hydrogen. Among all the surface-analytical tools currently available, ‘dynamic’ SIMS is the most favoured technique because it offers in-depth (three-dimensional) information with a combination of highest detection sensitivity (parts-per-billion) and excellent depth-resolution (down to less than 5 nm). However, these advantages of SIMS are counter-balanced by its strong ‘matrix effect’ [37, 38] i.e. the ionization probability of a given species varies by several orders of magnitude from one matrix to another, containing that particular species. Consequently, the secondary emission of a given ionic species is greatly affected by the instantaneous local surface chemistry of the sample. Since the ionization probability of a certain species is entirely matrix dependent, the secondary ion yield of that species has no straightforward relationship with the concentration of the species in the host, causing thereby a genuine hindrance to quantification. This phenomenon is known as the ‘matrix effect’ in SIMS. Compensation of the matrix effect is needed for quantification in SIMS and is possible by several methods such as calibration curve [39], ion implantation standards [40] etc. All these approaches need ‘standards’ with matrix composition close to that of the unknown sample. Moreover, it is very difficult to make compositional analysis of the interfacial regions using the above techniques. There is another technique known as ‘infinite velocity approach’ [41], which makes use of the high energy part of the secondary ions that are essentially unaffected by the instantaneous local surface chemistry. The major difficulty in this method is, however, the detection of high-energy secondary ions because of their extremely low count-rates compared to that of low-energy secondary ions.

### 3.1 Elemental Quantification and MCs$_{n}^{+}$ – SIMS

Irrespective of the mechanism of secondary ion formation, quantification in dynamic SIMS is universally accepted as the conversion of a secondary ion current $I^{\pm}(t)$ of a given species in a homogeneous target matrix, measured as a function of time $t$, to a concentration $C(z)$, measured as a function of depth $z$. Calibration of the depth scale is based on a strictly linear proportionality between the elapsed erosion time and the eroded depth of the sample, considering constant sputtering conditions throughout the measurement and consequently a fixed erosion rate. In reality, however, the linear time-to-depth mapping may not be strictly valid as the erosion by ion bombardment introduces smearing of depth information by both target atom relocation and surface topography development. But the major factor that hinders elemental quantification is the matrix effect. However, there exist certain techniques through which one can quantify a species of interest in the host matrix.

The most widely used technique for quantitative SIMS analysis depends on finding relative sensitivity factors (RSF) for a certain species. In order to determine the sensitivity factors, appropriate reference materials or ‘standards’ (the term is defined for materials whose composition has been determined by
independent means, either directly by analytical measurement or indirectly from the method of synthesis) are needed. The accuracy of the quantification obviously cannot be better than that of the standards. However, in developing a suitable standard, the greatest problem encountered is often to get an independent, artifact-free reference method that can be used to calibrate the SIMS method. The principal characteristics of a suitable standard for the determination of sensitivity factors for SIMS are

A. The composition should be homogeneous, both laterally and in depth since the sample layer eroded during determination of the intensity ratio may be quite shallow. It is also important to design the materials which allow the accurate measurement of erosion rates and the ion yields in the first few nm of a profile in order to establish the accuracy of the ultra-shallow profiling.

B. The composition should not be significantly altered during analysis by the effect of ion bombardment.

There are two simple approaches towards quantification using standards— the “calibration curve” and the “ion-implanted standards” method.

1. **Calibration curve method:**

This method relies on constructing a plot $I_x$ vs. the intensity of the detected species as a function of $C_x$, the respective elemental concentration for “standards” containing the species $x$ with various known concentrations [39, 42]. In order to keep the systematic uncertainties small, the sample to be measured must have a composition close to one of the standards used. The calibration curve of the species $x$ in a matrix can be different from the calibration curve obtained for the same species in another matrix. For the determination of the unknown concentration of a species, the calibration curve is used as an analytical curve, where $C_x$ is considered a function of $I_x$.

2. **Implantation standard method:**

This technique is much more accurate method for quantifying certain species present in a matrix [43,44]. In this method a “local standard” is prepared by implanting a controlled quantity of the species of interest with a known dose into a sample which should have the stoichiometry identical with that of the host matrix. By measuring the total fluence (dose) of the implanting species and the depth integral of the implant SIMS profile, RSF for the species $x$ in the host sample is determined. The estimated $(RSF)_x$ is then used to get the instantaneous concentration of the species in the matrix. The use of “implantation standards” for SIMS was first reported by Gittins et. al. [45] and has proven extremely useful for quantitative SIMS analysis of electronic materials. Such standards provide quantitative information on both the local solute concentration and on the distribution of the solute in the structure. One of the great advantages of this method is that the constituent of interest can be implanted directly into the near-surface region of an unknown sample to fabricate an in situ standard. Since the implanted dose is sufficiently small in comparison to the atomic density of the sample, the response characteristics of the sample are not altered because of the presence of the implant. The implanted dose is, therefore, subjected to the same chemical environment as the sample atoms, and the matrix effects should be identical to both.

Although quantification in a given matrix can be achieved by using standards with matrix composition as close as possible to the unknown sample, it is very complicated to quantify or even interpret the analysis across interfaces composed of matrices of different nature like metal/semiconductor, metal/polymer, metal/ceramic, etc. Some attempts have been made to correct point by point distortion of a...
depth profile across an interface due to the matrix effect by using a calibration curve [46, 47]. This calibration curve giving the variation of ion yield with matrix composition was previously established by carefully studying a set of samples with different compositions. There is no doubt that the accuracy of the calibration was seriously limited by the exact evolution of the matrix composition at each point and the linearity of the calibration curve. SIMS analysis under conditions of reduced or no matrix effect is certainly a better way to measure the distribution of elements across interfaces. The matrix effect depends largely on experimental conditions, namely the nature of the primary ion, the incident angle, the detected species and the energy of secondary ions.

3.2 MCs+ - SIMS for Compensation of ‘Matrix Effect’

Recent SIMS analysis with molecular MCs+ secondary ions has been found to be remarkable in making SIMS quantification possible without the aid of calibration standards. The technique is referred to as MCs+-SIMS [48, 49]. However, instead of Cs+ ions, other alkali ion bombardment and monitoring of MX+ ions (where X is an alkali primary ion, such as K+, Rb+, Na+, etc.) have also shown a similar reduced matrix effect [50]. The reduction (or absence) of matrix effect for these species was rationalized by their possible formation/ ionization mechanism, namely the combination of a neutral M atom with a Cs+ ion in the sputtering event. The implanted Cs atoms generally have very high ion yields (close to unity) and, in many cases, will be present as ions at the surface [51, 52]. Thus, under steady-state conditions the flux of MCs+ ions will reflect (via that of M atoms) the atomic concentration of the element M. It has been proved experimentally that for a variety of semiconductors the yield of these species exhibits a quadratic dependence on the polarizability $\alpha$ of the atom M, i.e. ion yield $\propto \alpha^n$ where $n=2$ [53], thus establishing the key role, which the polarizability of M plays in the formation of MCs+ molecular ions. Owing to the high potential applicability of this technique towards elemental quantification, a lot of work both theoretical and experimental have already been done in this field [54-63].

Although the MCs+ technique has found its applicability in direct quantification, it often suffers from a low useful yield particularly observed for the electronegative elements. In such cases, detection of MCs$_2$+ molecular ions offer a better sensitivity as the yield of MCs$_2$+ ions has been observed to be much higher than that of MCs+ ions by up to $10^2$ in certain cases [64]. Although several works have reported the mechanism of MCs+ formation, that of MCs$_n$+ ions (where $n = 1, 2$, etc.) still remains to be well understood.

3.2.1 MCs+ ions: Formation Mechanism and Characteristics
In a comprehensive study on positive and negative secondary ion yields of atomic and molecular species sputtered from elemental and compound targets under oxygen and cesium bombardment, Storms et al. [65] noted that diatomic species of the type MCs\(^+\), composed of a target specific element M and Cs from the primary ion beam, are sometimes emitted with surprisingly high yields, notably in the case of Zn. However, it was only until recently that this finding gathered attention when several groups reported on the usefulness of MCs\(^+\) ions, either for depth profiling of inert gases [66], which are known to exhibit a very low degree of ionization in SIMS, or for almost quantitative depth profiling of matrix and impurity elements in III–V semiconductors [48]. Particularly attractive was the observation that the MCs\(^+\) ion yields seem to depend very little on the matrix from which the element M is emitted [48]. This is in contrast to the severe “matrix effect” known from SIMS measurements involving oxygen or cesium bombardment and detection of atomic secondary ions.

![Graph](image_url)

**Fig. 3.** (a) Au depth profiles obtained under different experimental conditions for an Au layer (0.3 \(\mu\)m) deposited on a GaAs substrate. Condition (a) Au\(^+\) secondary ion under O\(_2^+\) bombardment. Condition (b) Au\(^+\) secondary ion with an off-set of 80 eV under O\(_2^+\) bombardment. Condition (c) Au under Cs\(^+\) bombardment. Condition (d) Au\(^+\) post-ionized under O\(_2\) bombardment. Condition (e) AuCs\(^+\) under Cs\(^+\) bombardment.

The application of the MCs\(^+\) technique becomes more useful when analyzing an interface of matrices of different natures, for instance the metal/semiconductor interface. Gao et al. [50] showed that a very simple structure of a thin (0.3 \(\mu\)m) gold over layer deposited on a GaAs substrate exhibited least matrix effect while monitoring the AuCs\(^+\) ions. The obtained profile did not exhibit any interface peak, which is characteristic of the typical matrix effect (Fig. 3).
Formation mechanisms of MCs\(^+\) secondary ions and the analytical applicability of MCs\(^+\)-SIMS technique have been thoroughly examined by several workers. Based on some experimental observations, it was proposed that an MCs\(^+\) ion forms via a recombination between an independently sputtered neutral M\(^0\) atom and a re-sputtered Cs\(^+\) ion in the close proximity of the sample surface. This process essentially makes the MCs\(^+\) species to suffer less from the matrix effect. Irrespective of the formation mechanism of MCs\(^+\) ions, it is obvious that the binding energy between M and Cs (either charged or neutral) plays a very important role in the formation of MCs molecule and the polarizability of M plays the key role in the binding strength of the two species. The fact that the emission intensity of MCs\(^+\) depends linearly with the atomic polarizability of M was established from the measurements of MCs\(^+\) ion yields from silicon containing various low-concentration elements [67]. The results showed that the ratio I(MCs\(^+\))/ I(SiCs\(^+\)) increased monotonically with the polarizability of M. Dependence of the binding strength on the polarizability can be modelled by an interaction potential between an alkali ion and a neutral atom M of the type (electropositive or electronegative with respect to the alkali element) [68]. In this case the attraction arises between the ion and the ion-induced dipole moment of the neutral species.

\[ \Phi^{(2)}(E, \theta) \propto D^{3/2} E^{-5} \cos^2 \theta \]  

(1)

Fig. 4: Yields of MCs\(^+\) ions sputtered from various elements as a function of the atomic polarizability of M. The solid line is a linear least-squares fit with n = 2.07 ± 0.20.

In order to fully explore the analytical applicability of the MCs\(^+\) technique, a thorough understanding of the formation mechanism of these molecular ions is needed. Gnaser and Oechsner [67] showed that for a variety of semiconductors the yield Y of these species exhibits a quadratic dependence on the polarizability (\(\alpha\)) of the atom M, i.e. \(Y \propto \alpha^n\) with \(n=2\). The experimentally established correlation between the yields and the polarizability was explained in a quantitative fashion by employing an appropriate interaction potential between Cs\(^+\) and M; the argument is based on a distribution function \(\Phi^{(2)}\) developed for the emission of small molecules in sputtering according to the double-collision scenario. For a dimer, this distribution function in the limit of large \(E\), is

\[ \Phi^{(2)}(E, \theta) \propto D^{3/2} E^{-5} \cos^2 \theta \]  

(1)
where $E$ and $\theta$ are the dimer’s emission energy and angle, respectively, and $D$ is its dissociation energy. The interaction between an alkali ion and a polarizable neutral atom (or molecule) can be successfully modelled by applying for the alkali ion-neutral atom interaction a potential of the form [68]

$$V(r) = Ar^{-12} - 0.5\alpha e^2 r^{-4}$$

(2)

where $r$ is the distance between the neutral atom and the ion, $\alpha$ is the polarizability of the former and $A$ is a constant which characterizes the repulsive term. The attraction is of the Langevin type and is that arising between the ion and the ion-induced dipole moment of the neutral species. Of particular concern is the depth of the potential well (i.e. the value of $V(r)$ at the equilibrium distance $r_m$), which is the dissociation energy $D$ for the MCs$^+$ molecule. The minimum of the potential is given by

$$D = V(r_m) \propto \alpha^{3/2} A^{-1/2}$$

(3)

Thus the dimer distribution function $\Phi^{(2)}$ will exhibit a dependence on the polarizability $\alpha$ given by

$$\Phi^{(2)} \propto \alpha^{3/2} A^{-3/2}$$

(4)

with an exponent for $\alpha$ ($n = 2.25$) which is very close to what has been observed experimentally (Fig. 4).

Clearly, the foregoing theoretical treatment includes some assumptions:

1. The interaction potential employed has been used successfully to describe gas-phase reactions, mostly at very high gas densities. (2) Its transferability to interactions occurring at the surface of a solid is not obvious.

On the other hand, the pronounced dependence on the polarizability found in the experiments indicates that the latter is a key parameter in any kind of formation mechanism of MCs$^+$. Studies on elemental and compound semiconductors (Si, Ge, InP, InSb, ZnSe, CdS, CdSe and CdZnTe) with Cs$^+$ fluences ranging from $2 \times 10^{15}$ cm$^{-2}$ up to saturation values ($> 1 \times 10^{17}$ cm$^{-2}$) reveal interesting emission characteristics of the molecular ions [69]. It has been observed that for all specimens with the exception of Si, the flux of MCs$^+$ ions scales linearly with the Cs$^+$ intensity over a wide range of cesium concentration (several orders of magnitude in some cases); for silicon deviations from this scaling are found at the highest Cs content and are tentatively ascribed to changes of the sputtering yield in the heavily doped Si specimens. The Cs$_2^+$/Cs$^+$ ratio, on the other hand, has been found to decrease more than linearly (possibly exponentially) upon reduction of the Cs concentration, indicative of a decreasing formation probability of Cs$_2^+$ dimers at low concentrations due to an increasing (average) distance between individual Cs atoms.

Theoretical studies carried out by Mootz et al. [70] show that MCs$^+$ ions have energy distributions, which are determined by the energy distributions of the sputtered neutral M atoms. For both distributions the mean emission energy is enhanced if the element’s surface binding energy is enhanced too. In contrast, the energy distributions of the re-sputtered Cs$^+$ ions appear to be element independent. The efficiency of MCs$^+$ molecule formation monitored by the MCs$^+$ signals is maximum for low mean emission energies and low surface binding energies. This shows the importance of a correlated emission of the partners forming the molecule. The formation mechanism of the MCs$^+$ clusters was investigated using a Monte Carlo model [71]. It was shown that the majority of the constituent particles of the formed clusters are initially first or second neighbour atoms at the surface and that the velocity distribution of the MCs$^+$ clusters becomes broader and peaked at higher velocities with increasing surface binding energy of the M atom. In addition, it was demonstrated that the interaction potential between the M and Cs$^+$ particle has no influence on the velocity distribution of the MCs$^+$ clusters. On the other hand, the cluster formation probability, defined as the probability that a sputtered M and Cs$^+$ particle will form a MCs$^+$ cluster, is
extremely sensitive to this interaction potential. It is also shown that the cluster formation probability decreases with increasing surface binding energy. Finally, a good correspondence is obtained between the calculated and experimental velocity distributions of MCs⁺ clusters sputtered from different monoatomic materials. As a consequence, the Monte Carlo model and the discussed results could be validated [71].

We have recently studied the combined effect of electropositive (cesium) and electronegative (oxygen) elements on the sputtered-ion emission from silver. Kinetic energy distributions of Cs⁺, Cs₂⁺, AgCs⁺ and AgCs₂⁺ ions measured at different oxygen pressures have exhibited changing slopes in their leading parts that hinted appreciable changes in the local instantaneous surface work function.

![Fig. 5: Normalized AgCs⁺ intensity as a function of Δφ.](image)

Integrated counts of AgCs⁺ showed an overall fall with increasing oxygen pressure. This observation apparently contradicts the concept for MCs⁺ molecular ions, as it is known that the formation of such molecular ions remains almost unaffected by the change in instantaneous local surface chemistry. This apparent discrepancy was answered by taking into account the exponential fall of re-sputtered Cs⁺ ions. Theoretically, the intensity of MCs⁺ molecular ions can be expressed as [69]

\[ I_{MCs^+} \propto Yc_M (1 - P_{M^-} - R_{M^+}) Yc_{Cs} P^+ f_{MCs^+} \]

where \( c_M \) is the concentration of M, \( Y \) is the global sputter-yield of the target, \( c_{Cs} \) is the surface cesium concentration, \( P^+ \) is the ionization probability of Cs and \( f_{MCs^+} \) is the formation probability for MCs⁺. \( P_{M^+} \) and \( P_{M^-} \) are the ionization probabilities for M⁺ or M⁻ secondary ions, respectively. For most practical purposes, \( P_{M^+} \) and \( P_{M^-} \) in the case of MCs⁺ ion intensities are negligible and all the factors except \( P^+ \) remains constant. \( f_{MCs^+} \), estimated at various oxygen exposures, has been found to be unchanged [63]. Hence Eq. (5) can be rewritten as

\[ I_{MCs^+} = K P^+ \]
where $K$ is a constant. In other words, the normalized MCs$^+$ intensity should show linear dependence on normalized Cs$^+$ intensity. The ionization probability $P^+$ depends on the ionization potential $I$ of the sputtered atom and surface work function $\phi$ according to the relation

$$P^+ \propto \exp\left[-(I - \phi)/\varepsilon_0\right] \quad (7)$$

where the parameter $\varepsilon_0$ is considered to depend on the normal component of the emission velocity of the secondary ions. However, some earlier observations [72] have confirmed its almost constant value for low emission velocities. Assuming the constancy in $\varepsilon_0$, if $\phi_i$ and $\phi_j$ are the two values of $\phi$, and $P_i^+$ and $P_j^+$ represent respective values of $P^+$, then from Eq. (7)

$$P_j^+ / P_i^+ \propto \exp[\Delta\phi / \varepsilon_0] \quad (8)$$

where $\Delta\phi = \phi_j - \phi_i$, the change in surface work function. Eq. (8) implies that the normalized integrated count should show an exponential dependence on $\Delta\phi$. The normalized Cs$^+$ count, plotted (Fig. 5) as a function of $\Delta\phi$, showed a very good agreement with the theoretical prediction for $\varepsilon_0 = 0.29$ eV. That is probably the first experiment to determine $\varepsilon_0$ for Cs$^+$. The normalized AgCs$^+$ intensity, plotted against normalized Cs$^+$ intensity, showed a linearity, which was in good agreement with the theoretical prediction for all oxygen pressures. This observation, even under a combined influence of electropositive and electronegative elements on the surface, strengthened the accepted concept that MCs$^+$ formation is essentially due to the combination of a neutral M$^0$ with a re-sputtered Cs$^+$ ion.

### 3.2.2 MCs$_2^+$ ions: Importance and Formation Mechanisms
Although MCs$^+$-SIMS technique has found its applicability in direct quantification, it generally suffers from a low useful yield. In such cases, detection of MCs$_2^+$ molecular ions offers a better sensitivity to that of MCs$^+$ ion (Fig. 6), as the yield of MCs$_2^+$ ions has been observed much higher than that of MCs$^+$ ions [50]. This is true in most of the cases where the elements are strongly electronegative with respect to cesium. Holliger et al. [73] investigated the analytical usefulness of monitoring MCs$_2^+$ ions for semiconductor profiling of n-type dopants such as P, Ge or As with a primary (Cs$^+$ beam) impact energy of 1 keV. They indicated that the MCs$_2^+$ technique has an advantage over the MCs$^+$ technique of providing higher useful yields for electronegative elements by up to 10$^2$ and can therefore be applied to perform more precise junction measurements in terms of concentration, dose, decay length and detection limit. The quantification of the impurities in GaN and AlGaN films by using the MCs$^+$ and MCs$_2^+$ ions enabled the detection of both electronegative and electropositive elements in the same analysis run. It was shown that the p-type dopant Mg and H could be measured together [74]. The detection limits of HCs$_2^+$, NCs$_2^+$ and MgCs$^+$ were reported at the same level as the limit of M ion detection. Further, the application of the MCs$^+$ and MCs$_2^+$ ions suppresses the matrix effect in the AlGaN/GaN films.

Although several works have reported the mechanism of MCs$^+$ ions [60,63,71,75-77], that of MCs$_2^+$ ions still remain to be well understood. In view of the fact that the kinetic energy distribution of a certain emitted species is an effective diagnostic to understand the formation mechanism of the species and its dynamics, a systematic study on the kinetic energy distributions (EDs) of MCs$_n^+$ (n = 0,1,2, . . . ) of species emerging from various metal targets under Cs$^+$ ion bombardment was reported to elucidate the probable formation mechanism of these molecular complexes. [67]. Several previous studies have investigated the energy distributions of MCs$^+$ ions [60,63,71,75-77] but corresponding data for MCs$_2^+$ appear to be lacking.

Earlier studies suggest the following three possible routes for the formation of these ions.

(i) \[ M + Cs^+ \rightarrow MCs^+ \]

(ii) \[ MCs + Cs^+ \rightarrow MCs_2^+ \]

(iii) \[ M^- + Cs^+ + Cs^+ \rightarrow MCs_2^+ \]

It was suggested that the first process seems dominant for electropositive elements, and for the electronegative elements, the other two processes ((ii) and (iii)) could become important in explaining the increased MCs$_2^+$ yield [71, 64]. Most of the earlier works tried to investigate the formation mechanism by studying the ion yields of MCs$_2^+$ ions with respect to that of MCs$^+$ ions. The fact that the changes in instantaneous surface chemistry has less effect on the secondary emission of MCs$^+$ and MCs$_2^+$ molecular ions was established from a work on secondary ion emission from copper under various Cs$^+$ primary energies and chamber pressures [78]. It was shown that under 3 keV Cs$^+$ energy, intensity of Cu increased with the gradual increase of oxygen pressure in the chamber exhibiting a typical matrix effect, whereas the intensities of CuCs$^+$ and CuCs$_2^+$ remained almost uninfluenced by the changes in the oxygen pressure. Another important observation was that for identical chamber pressure, the intensity of CuCs$_2^+$ always exceeded that of CuCs$^+$ at any impact energy [78], supporting the earlier observations that MCs$_2^+$ has a greater yield compared to MCs$^+$ ions. Since the emission intensity of Cs$_2^+$ ions is generally less than that of Cs$^+$ ions by orders of magnitude, it was argued that the formation of a CuCs$_2^+$ ion could not be due to direct recombination of a neutral Cu atom and a Cs$_2^+$ ion in the sputtering process. The formation of M Cs$_2^+$ was explained [79] to be due to a recombination of a sputtered M ion with two self-sputtered Cs$^+$ ions (i.e. process (ii)). Furthermore, Cs being electropositive with respect to Cu caused enhanced emission of Cu$^+$ ions under Cs bombardment thereby leading to increased yields of CuCs$_2^+$. 
Fig. 6. FCs$^+$ and FCs$_2$$^+$ ions profiles for a Si wafer implanted with fluorine at a dose of $8 \times 10^{15}$ atoms/cm$^2$.

The implantation peak concentration is at $2.5 \times 10^{21}$ atoms/cm$^3$.

Considering the fact that the kinetic energy distribution (EDs) of a certain species emitted in the SIMS process is an effective diagnostic to understand the formation mechanism of the species and its kinematics, energy distributions (EDs) of MCs$^+$ and MCs$_2$$^+$ molecular species have been made for various target materials under varying Cs environments [78-80]. Instantaneous local surface work functions estimated from the leading parts of the kinetic energy distributions were found to play a major role in the formation of these ion complexes. In the energy distributions of M, MCs$^+$ and MCs$_2$$^+$ ions for the elements Al, Cu and Ag for a typical bombarding energy of 2 keV, it was observed that for a given element the peak position of the ED shifted to lower values in the order M$^+$, MCs$^+$ and M Cs$_2$$^+$ ions (Fig. 5). This was found to be true for any value of impact energy. From the bombarding energy variations of EDs for M$^+$ or MCs$^+$ or M Cs$_2$$^+$, it was observed that the peak of the ED for each species shifted towards lower energy as the impact energy was increased [79]. The peak position of the energy distribution for any emitted species depends essentially on the surface binding energy (U) of the species as well as the surface work function ($\phi$), as understood by the simple expression

$$\text{Ion Yield} \propto \frac{E}{(E+U)^{\gamma}} \exp \left[ -\frac{(I - \phi)}{\varepsilon_0} \right]$$
The sublimation energy of pure Cs being much lower (0.83 eV) than that of the three metals, decrease of Cs concentration (i.e. increase of impact energy) should tend to increase the magnitude of the surface binding energy. Since this was contrary to what was actually observed in the study, the peak shift of the EDs towards lower energies was due to the increase of surface work function (due to lowering of Cs concentration with the increase of impact energy). The lower the work function, the greater is the shift of the energy distribution towards higher energies [81]. Any change in the instantaneous surface work function should reflect the variation of the leading edge profile of the energy distributions. By fitting tangents to the leading parts of the EDs and subsequently measuring the intercepts of the tangents with the energy axis one does the estimation of the work function changes. Fig. 7 shows the variation of the measured surface work function changes ($\Delta\phi$) with impact energies for $M^+$, $MCs^+$ and $MCs_2^+$ species, thus evidencing the role of surface work function changes on the energy distributions. The effect is more pronounced when the surface work function changes become more significant and this was demonstrated for silver by changing the impact angle of the incident beam [80].

Fig. 7. Surface work function change ($\Delta\phi$) versus impact energy for $Al^+$, $AlCs^+$ and $AlCs_2^+$ ions
The impact angle variation on the work function change was found to be more sensitive than the impact energy variation on the same. Fig. 8 shows the energy distributions of AlCs\textsuperscript{+} and AlCs\textsubscript{2}\textsuperscript{+} ions for different impact angles [71].

![Fig. 8. Energy distributions of AlCs\textsuperscript{+} and AlCs\textsubscript{2}\textsuperscript{+} ions for different impact angles.](image)

So far, a handful of works has been done to reveal the underlying formation mechanism of the MCs\textsubscript{2}\textsuperscript{+} molecular ions. The study of energy distributions of the MCs\textsubscript{2}\textsuperscript{+} molecules ions and its proposed constituents has been the key probe to understand its formation mechanism. The energy distribution of the MCs\textsubscript{2}\textsuperscript{+} molecules (where M = Zn, Cu, Ge, Ni and Mo) has been found to depend on the surface binding energy, which provides evidence that the energy distribution of the neutrals is also responsible for the MCs\textsubscript{2}\textsuperscript{+} distributions [70]. Furthermore, the narrower energy distribution of the trimers compared to respective dimers’ energy distribution supported a recombination of the constituents of the trimers subsequent to their sputter process. Comparison of the energy distributions of the components involved in the dimer formation process with the energy distributions of components, which might be responsible for
the trimer formation, strengthened the belief that the formation of an MCs\(^{2+}\) molecular ion was due to the recombination of MCs\(^{0}\) with Cs\(^{+}\) (process (iii)). The MCs\(^{0}\) occurring in this formation process results from the neutralization of an MCs\(^{+}\) ion by electronic capture [76]. In another study of MCs\(_{n}^{+}\) molecular ions formation from silver surface under a varying oxygen environment, a linear dependence of AgCs\(^{2+}\) intensity on the ionization probability of Cs\(^{+}\) (Fig. 9) suggested that an AgCs\(^{2+}\) molecular ion forms via the recombination of AgCs\(^{0}\) and Cs\(^{+}\) [63]. Furthermore, the estimated mean emission energies of various species also indicated that the formation of MCs\(^{2+}\) via process (iii) seemed to be the most probable one in that particular case. A quantitative evaluation of the respective mass signals, with respect to the spatial and temporal correlation of the components forming the molecule, corroborated the fact that in the case of the MCs\(^{2+}\) formation the spatial and temporal correlation is one order of magnitude higher than that in the MCs\(^{+}\) formation process [70]. Besides, it was observed that in both the cases of dimer and trimer formation, the spatial and temporal correlation decreases with increasing surface binding energy.

To explore the enormous quantitative potential of the MCs\(_{n}^{+}\), in recent times, several experiments have been reported where dual beam have been successfully used to improve the MCs\(_{n}^{+}\) signal. In a “Cesium-Xenon” co-sputtering experiment, performed on pure silicon, silicon oxide and aluminum oxide, MCs\(_{n}^{+}\) clusters’ signals were reported to enhance significantly for a Cs beam concentration, with maxima that varied from 10% to 30% [82] and the data relative to the silicon wafer were successfully interpreted by models derived from the tunnelling model. To optimize the advantageous quantification technique consisting in analyzing MCs\(_{n}^{+}\) clusters, Writz et al. have developed the Cation Mass Spectrometer (CMS), a new instrument especially dedicated to perform this kind of analysis [83]. In this novel technique, collimated and adjustable stream of neutral Cs atoms are deposited on the surface of the sample while this one is being bombarded with X\(^{+}\) (where ‘X’ stands for any element excepting Cs). This experimental technique permits a successful decoupling of the sputtering and Cs introduction processes by avoiding the constraints imposed by an energetic Cs\(^{+}\) ion bombardment. As a consequence, it becomes possible to optimize simultaneously the sensitivity of the analysis, by carefully adjusting the Cs concentration to its optimum value, and the depth resolution of the analysis, by choosing adequate primary bombardment conditions. For three samples (Al, Si and Ni) covering an important range on the work function scale (\(\phi = 4.28–5.15\) eV), it has shown that the behavior of the useful yields of the detected MCs\(_{n}^{+}\) signals only depends on the ratio between the erosion and deposition rates, but not on the individual values of these two rates. This characteristic becomes very important within the perspective of a low-energy primary bombardment with a view to an improvement of the depth resolution. Furthermore, the deposition of neutral cesium has been reported to reduce the work function of the sample that increases the useful yields significantly and helps avoiding the matrix effect for elements with high electron affinity [84].

4. SiGe Alloys: Growth and Compositional Analysis

Germanium incorporation in silicon leaves the nature of silicon band structure intact for concentrations up to 85%, but produces significant reductions in the band gap energy and in the electron and hole effective masses, thus enabling the SiGe alloys to be extensively usable for their electrical properties. SiGe alloy has the same crystallographic structure as Si (over the entire composition range) but its lattice constant is larger by 4.2% compared to that of pure Si. However, epitaxial growth technologies have made the growth of coherent Si\(_{1-x}\)Ge\(_{x}\) structures possible where the in-plane SiGe lattice spacing exactly matches that of Si. Despite the fact that the main commercial heterostructure based on SiGe is the heterojunction bipolar transistor (HBT), the complementary metaloxide-semiconductor (CMOS) research has also focused on the use of SiGe material for boosting the performances. New applications for CMOS are emerging that are based on the crystalline properties of the SiGe material: strained devices, high-
mobility SiGe channel transistors or architectures where it is used as a sacrificial layer. Application of the SiGe compound semiconductor in the context of CMOS technology enables solutions based on the trade-off between performance and cost. As SiGe is just one step ahead of Si, the mature silicon technology with highly developed arsenal of tools and well established processing is at hand being fully compatible with new schemes and design platforms in which the compound semiconductor and silicon co-exist. By changing the alloy composition the electrical and optical properties can be modified at will via so-called band gap engineering to meet the requirements of a particular application. Introducing additional strain and enhancing the charge carrier mobility via Si/SiGe heterostructure architecture enables those applications in which traditionally III-V’s dominate to migrate nowadays to SiGe and low-power CMOS technologies delivering appropriate performance at much lower cost.

SiGe layers are already used as source/drain (S/D) regions to induce uniaxial compressive stress in the Si channel, which results in the enhancement of hole mobility in p-type metal-oxide-semiconductor (PMOS) [85]. An alternative method for the formation of shallow strained SiGe S/D regions consists in selectively depositing a pure Ge layer on a Si substrate followed by the Ge-Si interdiffusion induced by a subsequent anneal [86,87]. The optimization of such a technology requires the precise evaluation of the Ge concentration in the full range of composition and the understanding and control of the Ge-Si interdiffusion phenomenon.

The most appropriate analytical technique with highest detection sensitivity (subparts per billion) for measuring impurity concentrations is SIMS [88-97]. However, strong compositional dependence of the secondary ion yield has always made quantification in SIMS a painstaking job. When the concentration of the analyzed element becomes too high with respect to the reference material (Si in the present work), matrix effects may be observed thereby degrading the reliability of the measured SIMS profiles strongly [98-102]. This is the case with Si$_{1-x}$Ge$_x$ layers, in which matrix effects are systematically observed under conventional SIMS experimental conditions. These effects increase with the Ge atomic fraction. They are, however, reported to be small for Ge concentrations lower than 30 at. % [98-99]. Many solutions have been proposed to reduce and/or suppress them, such as the use of an O$_2$ primary ion beam at normal incidence [103,104]. In the case of an inclined O$_2$ beam, a reduction of matrix effects for Ge atomic fractions up to 50 at. % has also been reported, provided the impact energy is lower than 3 keV [102, 105]. For higher Ge contents, the detection of $^{74}$Ge$^{76}$Ge secondary ions under Cs$^+$ bombardment considerably reduces matrix effects. They are, however, not completely suppressed for very high Ge concentrations (60 at. %) [102]. Furthermore, primary ion energy influences the apparent sharpness of the Si$_{1-x}$Ge$_x$ layers during the compositional analysis of such samples [106-108].

Secondary polyatomic ions, such as $^{28}$Si$^{70}$Ge clusters under O$_2$+ bombardment have also been used for Ge concentration profiling [101]. Recently, germanium quantification using negative ion detection in ToF-SIMS has also been investigated [109]. Although a fair linear correlation between ion ratios and Ge/Si layer composition ratios was found, nonlinear behaviour was still present for Ge concentration higher than 50%, hampering the precision of analysis. Although, the “full-spectrum method”, as an alternative protocol, was investigated, the practical difficulty was in simultaneous monitoring of more than 25 ionic species at one time, with sufficient mass resolution to be able to separate possible interferences [109].

The MCs$^+$-SIMS has been successfully used for the analysis of Ge concentration upto 23.5% [110] in SiGe alloys. Quantification in the higher range of Ge concentration in SiGe at low sputtering energies was also reported using MCs$^+$ [111-113]. However, reliable results of analysis with MCs$^+$-SIMS method have not been reported so far for SiGe layers with Ge contents higher than 50 at.%. The present section reports a thorough investigation on the use of MCs$^+$-SIMS method for the quantification of germanium concentration in Si$_{1-x}$Ge$_x$ ($0 < x < 0.72$) in a broad range of Cs$^+$ impact energies demonstrating the
complete suppression of matrix effect in SIMS quantification. The novel methodology has successfully been applied for direct compositional analysis of an MBE-grown Si/Ge superlattice structure.

4.1 SiGe Alloy Film Deposition

SiGe alloy samples (SG1, SG2, SG3, SG4, etc.) with increasing germanium content were grown using molecular beam epitaxy (MBE) system. For all samples, a 100 nm Si buffer layer was grown on cleaned Si(100) substrates at 750°C prior to alloy film deposition. Si was evaporated by an e-gun at a rate of 0.1 nm/s. Ge effusion cell temperature was varied so as to achieve various deposition rate. Substrate temperature and rotation speed were 750°C and 3 rpm, respectively during deposition. The base pressure of the growth chamber was 2.5 × 10^{-10} torr.

4.2 Characterization of SiGe Alloy

Surface morphology of the deposited alloy films was studied using ex situ ambient AFM in contact mode. Scans were performed over several regions of the films for different scan areas. Typical AFM topographic images (3 × 3 μm²) of four films with corresponding height distributions are shown in Fig. 10. As evident from the images, the morphology of SG1 shows pronounced roughness, with estimated top roughness ~ 2.1 nm. However, the top roughness for SG2, SG3 and SG4 were much less and were found to decrease with increasing germanium content. The estimated top roughnesses were 0.14 nm, 0.13 nm and 0.10 nm for SG2, SG3 and SG4, respectively.

Fig. 10: AFM topographic images (5 μm × 5 μm) of (a) SG1, (b) SG2, (c) SG3 and (d) SG4. Inset: corresponding height distributions.
In order to evaluate the spatial distribution of silicon and germanium atoms in the deposited alloy films, the x-ray elemental mapping was performed using the EDAX energy dispersive x-ray spectrometer with electron acceleration at 10 kV that sets a probe diameter of about 4 nm. The sample was tilted at an angle of 70° with respect to the electron beam. Such low acceleration voltage and oblique incidence of the electron beam with respect to the sample surface brings the depth of x-ray generation more toward the surface of the probed sample making the EDS technique surface sensitive. Consequently, the silicon and germanium atoms confined within a few hundred nanometres from the surface of the present SiGe alloy films can be detected efficiently. The typical x-ray micrographs obtained for SG3 reveals that of both silicon and germanium are homogeneously distributed over the alloy films. There is no sign of segregation of the constituent elements in the alloy films.

![Figure 11: EDS spectrum of SiGe alloy film. Inset: Comparison of normalized EDS spectra for various Si$_{1-x}$Ge$_x$ films.](image)

Figure 11 shows a typical EDS spectrum of deposited SiGe alloy film. For comparison, we have normalized the individual EDS spectrum by the corresponding silicon K$_\alpha$ intensity. The normalized EDS spectra (inset; Fig. 11) show that the germanium L$_\alpha$ signal intensity increases monotonically with increasing germanium content of alloy films. The quantitative analysis was performed with a thin film standardless software program using the characteristic x-ray line of each element. EDS patterns were taken at various parts of the samples chosen randomly and it was found that the composition of the alloy films are very uniform for all the samples.

In order to check the crystallinity of the deposited alloy films, x-ray diffraction (XRD) measurements were carried out at the Indian Beamline, BL-18B at Photon Factory in Tsukuba, Japan. The sample was illuminated by x-ray beam with wavelength $\lambda$=1.08887Å. The sample was mounted horizontally on an 8-circle goniometer (Huber, Germany) at the focal point of the focusing mirror of the beamline. The scattered x-ray beam was collected by a single channel scintillation detector mounted at a distance of 380 cm on to the 2θ arm of the goniometer. A slit of dimension 1.5 mm (horizontal) x 0.25 mm (vertical) was mounted prior to the detector to increase the signal-to-background ratio. The slit settings were kept unaltered for all diffraction and reflectivity (XRR) measurements. Figure 12 shows a typical XRD pattern
of the alloy samples around Si (400) peak of the substrate observed at 23.63°. The less intense peak in the low theta region of the XRD pattern corresponds to the deposited Si$_{1-x}$Ge$_x$ alloy layer. Since the lattice parameter of germanium is larger (4.2%) than that of silicon, the alloy peak shifts towards low theta direction with increasing germanium content as the lattice parameter of Si$_{1-x}$Ge$_x$ alloy increases with $x$.

The epitaxial nature of the grown alloy films were also checked with high resolution cross-sectional TEM (HR-XTEM). Figure 13 show the HR-XTEM images of a typical alloy film (SG4). Fig. 13a shows the growth of SiGe alloy film (~ 250 nm) on the top of Si(100) buffer layer (~100 nm). The HR-XTEM image (Fig. 13b) clearly depicts epitaxial nature of SiGe alloy layers grown on Si(100). The lattice constant SiGe alloy obtained from HR-XTEM study showed good agreement with that obtained from XRD measurement.

In order to measure SiGe alloy layer thickness, SIMS depth profile was carried out. 3 keV Cs$^+$ primary ions was used for conventional SIMS depth profile measurement and negative secondary ions (Si$^-$ and Ge$^-$) were monitored. Primary ion current was kept fixed at 60 nA. The primary beam was rastered over a region of 1000×1000 $\mu$m$^2$ while secondary ions were collected from a region of 200×200 $\mu$m$^2$ located at the center of the rastered area. Depth of the erosion crater was measured using a surface profilometer. Typical SIMS depth profiles of Si and Ge in an alloy film have been shown in Fig. 14. As seen in Fig. 14
that the typical thickness of the deposited alloy layers were \( \sim 170 \) nm and \( \sim 250 \) nm for SG1 and SG4, respectively. Thickness of the alloy films obtained from SIMS measurement also showed a very good agreement with what obtained from HR-XTEM. Higher Ge intensity obtained for SG4 signifies the existence higher Ge content in alloy film as compared to SG1. It is also evident from the SIMS depth profiles that the alloy composition is homogeneous over the depth of the film. However, the interface broadening occurs due to the in-diffusion of germanium into the silicon buffer layer, which is possibly due to the effect of elevated temperature during growth of the alloy films.

Fig. 14: SIMS depth profiles of SG1 and SG4 using 3 keV Cs\(^+\).

### 4.3 Matrix Effect Compensation and Direct Composition Analysis

For MCs\(^+\)-SIMS study the samples were bombarded with 1-5 keV Cs\(^+\) primary ions while the beam current was kept fixed (60-150 nA). The impact angle was 75° with respect to surface normal. Both SiCs\(^+\) and GeCs\(^+\) signals remained steady over the entire film indicating a homogeneity in composition of the grown alloy films. The MCs\(^+\) intensity for a species M is given by [69]

\[
I_{\text{MCs}^+} \propto Y_{cM} Y_{C} P^+ f_{\text{MCs}^+},
\]

where \( Y \), \( P^+ \) and \( f_{\text{MCs}^+} \) are the total sputtering yield, ionization probability of cesium and formation probability of MCs\(^+\) molecular ions, respectively. \( c_M \) and \( c_C \) are the fractional surface concentrations of the species M and cesium, respectively. Considering the constancy of the formation probability \( f_{\text{MCs}^+} \) [114] for both germanium and silicon, Eq. 9 can be rewritten as

\[
I_{\text{GeCs}^+} / I_{\text{SiCs}^+} = K c_{\text{Ge}} / c_{\text{Si}}
\]

where \( K \) is a constant and can be treated as the ‘relative sensitivity factor’ (RSF) for compositional analysis using MCs\(^+\)-SIMS approach.

Figure 15 depicts the variation of \( I_{\text{GeCs}^+} / I_{\text{SiCs}^+} \) as a function of \( c_{\text{Ge}} / c_{\text{Si}} \), obtained from EDS, for various impact energies. The linearity of the curves, irrespective of germanium and silicon contents, for all impact energies clearly reveals the absence of ‘matrix effect’ even for high germanium concentration. Whereas, some earlier studies reported the absence of matrix effect for impact energy lower than 1 keV and germanium content less than than 50% [113]. Compensation of the matrix effect irrespective of impact energy in our case can be attributed to low steady-state surface concentration of cesium due to larger
primary impact angle. The ratio of the formation probabilities of SiCs+ and GeCs+, in the present case, remains constant for the entire germanium concentration range while apparently the same varies in the other cases. The “matrix effect minimization” for all possible Si1-xGex compositions in the present case could be due to the lower steady state cesium surface-concentration because of relatively higher sputtering yield of the target material under 75° impact angle.

Figure 15 shows the monotonic increase of the RSF’s with bombarding energies. The RSF’s have been obtained through fitting of \( \frac{I_{\text{GeCs}^+}}{I_{\text{SiCs}^+}} \) data points with a straight line. Although RSF shows an increasing tendency with impact energy, it is always advisable to use low impact energy to ensure less beam-induced surface damage yielding improved depth resolution. However, it can be safely stated that for all practical
analytical purposes low impact energy can be used without compromising elemental sensitivity, since the increasing trend of RSF with impact energy is inappreciable (Fig. 16).

4.3 Compositional Analysis of Si/Ge Multilayers

Having discussed the potential of MCs$^+$-SIMS for complete suppression of matrix effect and the calibration procedure of the MCs$^+$ intensity, we now show application of this methodology for direct compositional analysis of an MBE grown typical Si/Ge multilayer structure. For this purpose ten successive Si/Ge bilayers were grown on a Si buffer layer of 750 Å and a Si cap layer of 330 Å was deposited on the top. During sample growth, the substrate (Si (001) wafer) was kept at 400°C and the deposition rate for both Si and Ge was 0.5 Å/sec. The details of sample preparation were discussed elsewhere [115].

![SIMS depth profile 10 Si/Ge bilayers using 2.5 keV oxygen.](image1)

Fig. 17: SIMS depth profile 10 Si/Ge bilayers using 2.5 keV oxygen.

![Concentration profiles of Ge and Si as obtained from MCs$^+$ SIMS. The right hand scale represents the corresponding GeCs$^+$ and SiCs$^+$ signal intensities.](image2)

Fig. 18: Concentration profiles of Ge and Si as obtained from MCs$^+$ SIMS. The right hand scale represents the corresponding GeCs$^+$ and SiCs$^+$ signal intensities.

For conventional SIMS-depth profiling, the sample was irradiated using 2.5 keV O$^+$ primary ion beam with primary ion current 120nA. Figure (Fig. 17) clearly depicts the presence of ten Si/Ge bilayers. The typical Si/Ge bilayer thickness was found to be ~ 90 nm. This thickness shows nice agreement with that
independently obtained from XRD. The difference in intensity variation between Si\(^-\) and Ge\(^-\) would possibly be due to the difference in the ion yield of these species.

MCs\(^+\)-SIMS analysis has been performed under Cs\(^+\) bombardment with an impact energy of 1.5 keV and impact angle of 75\(^\circ\). A low primary current of 50 nA was used in order to achieve low erosion rate and thereby high depth resolution. The primary beam was rastered over a region of \(1000\times1000 \text{ \(\mu\)m}^2\) and MCs\(^+\) ions were collected from the central region \((200\times200 \text{ \(\mu\)m}^2)\) of the rastered area. Depth of the erosion crater was measured at the end of analysis. Variation of both GeCs\(^+\) and SiCs\(^+\) intensity (Fig. 18) clearly exhibits the existence of ten Si/Ge bilayers. The depth \((z)\) distributions of Ge and Si concentration \(c_{\text{Ge}}(z)\) and \(c_{\text{Si}}(z)\) (Fig. 18) have been determined from the intensity ratio of GeCs\(^+\) and SiCs\(^+\) clusters utilizing the methodology described in the previous section.

![Figure 19: Electron density profile of 10 Si/Ge bilayers as obtained from XRR (blue solid line) and MCs\(^+\) - SIMS (red circles). Two vertical dashed lines indicate expected buffer and cap layers.](image)

Using the concentration profiles obtained through MCs\(^+\)-SIMS approach we have extracted the electron density profile \(\rho_e(z)\) of the multilayer applying the expression

\[
\rho_e(z) = N_A \sum_{M=\text{Ge, Si}} \frac{Z_M c_M(z)}{A_M}
\]

where \(N_A\), \(Z_M\), \(c_M(z)\) and \(A_M\) are the Avogadro number, atomic number, concentration profile and mass number of the constituent element M (Ge and Si), respectively. The extracted EDP (Fig. 19) of the multilayer sample has been compared with that independently obtained from XRR and is found to be in close agreement, demonstrating the potential applicability of MCs\(^+\)-SIMS approach in quantitative composition analysis of Si/Ge superlattice and SiGe alloys structures [116].

5 Conclusion:

MCs\(_n\)\(^+\) molecular ions have great relevance in suppressing ‘matrix effect’ arising in secondary ion mass spectrometry (SIMS) analysis because of their significant insensitivity to the changes in sample surface
chemistry. Consequently, the knowledge about formation mechanisms of these molecular species is of immense importance for optimal application of MCs\textsuperscript{n}+ SIMS technique in material analysis. Compared to that, very few reports exist on plausible formation mechanisms of MCs\textsuperscript{n}+ molecular ions. The work described in this paper is an effort to study the role of impact parameters and surface environment on the formation of MCs\textsuperscript{n}+ molecular ions under SIMS process. We have shown that the formation of MCs\textsuperscript{+} ions via recombination of neutral M\textsuperscript{0} atoms with resputtered Cs\textsuperscript{+} ions seems to be unquestionable. However, MCs\textsuperscript{2+} formation via recombination of neutral M\textsuperscript{0} with Cs\textsuperscript{2+} or neutral MCs\textsuperscript{0} with Cs\textsuperscript{+} appear to be independently viable depending on the nature (electropositivity or electronegativity) of the element M and the surface environment where the formation actually takes place. We have also demonstrated the potential of the MCs\textsuperscript{n}+-SIMS technique for complete suppression of matrix effect arising in the SIMS analysis of SiGe alloys and have successfully employed this novel methodology for quantitative depth profiling of Si/Ge multilayered structures.

References

[1] Czanderna AW. Methods of Surface Analysis. New York: Elsevier; 1975.
[2] Werner HW, Garten and R. P. H. Rep. Progr. Phys 1984; 47, 221.
[3] Oechsner H, Thin Film and Depth Profile Analysis: Topics in Current Physics. Vol. 37. Berlin: Springer; 1984.
[4] Hofmann S. Practical Surface Analysis with AES and XPS., Chapter 4: Depth Profiling., Chichester: Wiley; 1990.
[5] Hofmann S. Surf. Interface Anal 198; 2: 148.
[6] Hofmann S. J. Vac. Sci. Technol. A 1991; 9: 1466.
[7] Hofmann S, Surf. Interf. Anal.1986; 9: 3.
[8] Oechsner H, Vacuum 1987; 37: 763.
[9] Hondros ED, Seah MP, Hofmann S, Lejcek P. Interfacial and surface microchemistry Physical Metallurgy 4th edn, chapter 13, Amsterdam: Elsevier;1996, p 1201.
[10] Honig RE. Thin Solid Films 1976; 39: 3.
[11] Benninghoven A, Thin Solid Films 1976; 31: 89.
[12] Hofmann S. Appl. Phys.1976; 9: 59.
[13] Hofmann S. Progr. Surf. Sci.1991; 36: 35.
[14] Riviere JC, Surface Analytical Techniques, Oxford:Clarenon;1990.
[15] Behrisch R, Sputtering by Ion Bombardment , Vol. I, Heidelberg,: Springer Verlag; 1981 and Vol. II, Heidelberg: Springer Verlag; 1983.
[16] Benninghoven A, Rudenauer FG, Werner WH. Secondary Ion Mass Spectrometry: Basic Concepts, Instrumental Aspects, Applications and Trends. New York:Wiley; 1987.
[17] Hofmann S. Appl. Surf. Sci. 1993; 70:71 9.
[18] Dowsett MG, Smith NS, Bridgeland R, Richards D, Lovejoy AC, Pedrick P. Proc. SIMS X ed A Benninghoven et al, Chichester: Wiley;1996.
[19] Iltgen K, Niehuis E, Bendel C, Benninghoven A. J. Vac. Sci. Technol. A 1997; 15; 460.
[20] Hofmann S. Surf. Interface Anal.1994; 21; 304.
[21] Hofmann S. J. Surf. Anal. 1996; 2; 79.
[22] Hofmann S. J. Surf. Anal. 1997; 3; 389.
[23] Hofmann S. Vacuum 1997; 48; 607.
[24] Hofmann S. J. Surf. Anal.1998; 4; 9.
[25] Dowsett MG, Barlow RD. Anal. Chim. Acta 1994: 297; 253.
[26] Kitada T, Harada T, Tanuma S. Appl. Surf. Sci.1996: 100-101; 89.
[27] Gautier B, Prost R, Prudon G, Dupuy JC. Surf. Interface Anal. 1996; 24: 733.
[28] Herzog RFK, Vichhoeck F. Phys. Rev. 1949: 76; 855.
[29] Honig RE. J. Appl. Phys. 1958: 29; 549.
[30] Liebl H. J. Appl. Phys. 1967: 38; 5277.
[31] Werner HW. Vak.-Tech. 1968: 17; 37.
[32] Benninghoven A. Phys. Status Solidi 1969: 34; 196.
[33] Ronshheim PA. Appl. Surf. Sci. 2006: 252; 7201.
[34] Magee CW, Hockett RS, Buyuklimanli TH, Abdelrehim I, Marino JW. Frontiers of Characterization and Metrology for Nanoelectronics 2007; AIP.
[35] Buyuklimanli TH, Magee CW, Marino JW, Walther SR. J. Vac. Sci. Technol. B 2006: 24; 408.
[36] Meuris M, Bisschop PD, Vandervorst W. Jackman JA. Proc. SIMS VII, John Wiley; 1990.
[37] Wilson RG, Stevie FA, Magee CW. Secondary Ion Mass Spectrometry: A Practical Handbook for Depth Profiling and Bulk Impurity Analysis, New York: John Wiley; 1989.
[38] Chakraborty P. Ion Beam Analysis of Surfaces and Interfaces of Condensed Matter Systems (Ed: Purushottam Chakraborty) New York: Nova Science; 2002).
[39] Werner HW. Surf. Interface Anal. 1980: 2; 56.
[40] Gittins RP, Morgan DV, Dearnaley G. J. Phys. D 1972: 5; 1654.
[41] Wittmaack K. Surf. Sci. 1999; 429; 84.
[42] Werner HW, Boudewijin PR. Vacuum 1984: 34; 83.
[43] Williams P. Practical Surface Analysis, Vol. 2, New York: Wiley; 1990.
[44] Werner HW. Acta Electronica 1976: 19; 53.
[45] Griffins RP, Morgan DV, Dearnaley G. J. Phys. D 1972: 5; 1654.
[46] Galuska AA, Morrison GH. Int. J. Mass Spectrom. Ion Processes 1984: 61; 59.
[47] Gao Y, Harmand JC. J. Vac. Sci. Technol. A1988: 6; 2243.
[48] Gao Y. J. Appl. Phys. 1988: 64; 3760.
[49] Magee CW, Harrington WL, Botnick EM. Int. J. Mass Spectrom. Ion Proc. 1990: 103; 45.
[50] Gao Y, Marie Y, Saldi F, Megion HN. Int. J. Mass Spectrom. Ion Proc. 1995:143; 11.
[51] Ortega JE, Oellig EM, Ferron J, Miranda R. Phys. Rev. B 1987; 36; 6213.
[52] Schroer J, Gnaser H, Oechsner H. Proc. SIMS IX. New York: Wiley; 1993.
[53] Gnaser H, Oechsner H. Surf. Sci. Lett. 1994; 302; L289.
[54] Mootz T, Block W, Migeon HN. Secondary Ion Mass Spectrometry, SIMS XI. New York: Wiley; 1997.
[55] Ecker P, Bieck W, Ruiz-Lopez MF. Secondary Ion Mass Spectrometry, SIMS XII. New York: Wiley; 1999.
[56] Meyer S, Staudt C, Wucher A. Appl. Surf. Sci. 2003: 203-204; 48.
[57] Writz T, Migeon HN, Scherer E. Appl. Surf. Sci. 2003: 203-204; 189.
[58] Gnaser H. Surf. Interf. Anal. 1996: 24; 483.
[59] Gnaser H. Surf. Sci. 1995: 342; 319.
[60] Gnaser H, Oechsner H. Surf. Interf. Anal. 1994: 21; 257.
[61] Bock W, Gnaser H, Oechsner H. Anal. Chem. Acta 1994: 297; 277.
[62] Gnaser H. J. Vac. Sci. Technol. A 1994: 12; 452.
[63] Saha B, Sarkar S, Gnaser H, Chakraborty P. Surf. Sci. 2008: 602; 1061.
[64] Gao Y, Marie Y, Saldi F, Migeon HN. Secondary Ion Mass Spectrometry, SIMS IX. New York: Wiley; 1994; p 382.
[65] Storms H, Brown KF, Stein JD. Anal. Chem. 1977: 49; 2023.
[66] Ray MA, Baker JE, Loxton CM, Greene JE. J. Vac. Sci. Technol. A. 1988: 6; 44.
[67] Gnaser H, Oechsner H. 1994: Surf. Sci. Lett.; 302; L289.
[68] Bloom S, Margenau H. Phys. Rev. 1985: 85; 670.
[69] Gnaser H. Surf. Sci. 1995: 342; 319.
[70] Mootz T, Adriaens A, Adams F. Int. J. Mass Spectrom. IonProcess. 1996: 156; 1.
[71] Vlekken J, D’Olieslaeger M, Knuyt G, Vandervorst W, Schepper LD. J. Am. Soc. Mass Spectrom. 2000: 11; 650.
[72] Yu ML. Phys. Rev. Lett.1981: 47; 1325.
[73] Holliger P, Laugier F, Dupuy JC. Surf. Interface Anal. 2002: 34; 472.
[74] Brizon J, Conard T, Vandervorst W, Houssiau L. Appl. Surf. Sci. 2004: 231–232; 749.
[75] Mootz T, Adams F. Int. J. Mass Spectrom. Ion Process. 1996: 152; 209.
[76] Mootz T, Adriaens A, Adams F. Int. J. Mass Spectrom. Ion Process. 1997: 163; 197.
[77] Gnaser H. Proc. SIMS XI, Chichester: Wiley; 1998, p. 915.
[78] Sarkar S, Chakraborty P. Nucl. Instr. and Meth. B 2003: 212; 364.
[79] Sarkar S, Chakraborty P, Gnaser H. Phys. Rev. B 2004: 70; 195427.
[80] Sarkar S, Chakraborty P. Nucl. Instr. and Meth. B 2005: 232; 153.
[81] Wang YL. Phys. Rev. B 1988: 38; 8633.
[82] Hongo C, Tomita M, Suzuki M. Appl. Surf. Sci. 1999: 144–145; 306.
[83] Writz T, Migeon HN. Surf. Sci. 2004: 557; 57.
[84] Philipp P, Writz T, Migeon HN, Scherrer H. Appl. Surf. Sci. 2006: 252; 7205.
[85] S. E. Thompson, M. Armstrong, C. Auth, S. Cea, R. Chau, G. Glass, T. Hoffman, J. Klaus, Z. Ma, B. Mcintyre, A. Murthy, B. Obradovic, L. Shifren, S. Sivakumar, T. Ghanie, K. Mistry, M. Bohr and Y. El-Mansy, IEEE Electron Dev. Lett. 25, 191 (2004).
[86] Ranade P, Takeuchi H, Subramanian V, King TJ. IEEE Electron Device Lett.2002: 23; 218.
[87] Ranade P, Takeuchi H, Lee WC, Subramanian V, King TJ. IEEE Trans. Electron Devices 2002: 49; 1436.
[88] Kube R, Bracht H, Hansen JL, Larsen AN, Haller EE, Paul S, Lerch W. J. Appl. Phys. 2010: 107; 073520.
[89] Marona L, Perlin P, Czernecki R, Leszczyński M, Bockowski M, Jakiela R, Suski T, Najda SP. Appl. Phys. Lett. 2011: 98; 241115.
[90] Liu X, Morris RJH, Myronov M, Dobbie V, Leadley DR. J. Phys. D: Appl. Phys.2012: 43; 505303.
[91] Cui Y, Yin S, Wang D, Xing G, Leng S, Wang R. J. Appl. Phys. 2010: 108; 104506.
[92] Napolitani E, Salvador DD, Storti R, Carriera A, Mirabella A, Priolo F. Phys. Rev. Lett.2004: 93; 055901.
[93] Caccavale F, Chakraborty P, Quaranta A, Mansour I, Gianello G, Bosso S, Corsini R, Mussi G. J. Appl. Phys. 1995: 78; 5345.
[94] Bracht H, Haller EE, Clark-Phelps R. Phys. Rev. Lett. 1998: 81; 393.
[95] Boger R, Fiederle M, Kirse L, Maier M, Wagner J. J. Phys. D: Appl. Phys. 2006: 39; 4616.
[96] Chu DP, Dowsett MG. Phys. Rev. B 1997: 56; 15167.
[97] Koumetz S, Ketata K, Ketata M, Marcon J. J. Phys. D: Appl. Phys.1998: 31; 3421.
[98] Jackman JA, Dignard-Bailey L, Storey RS, Mac-Pherson C, Rolfe S, Van Der Zwan L, Jackman TE. Nucl. Instrum. Methods in Phys. Res. B 1990: 45; 592.
[99] Zalm PC, Vriezema CJ, Gravesteijn DJ, van de Walle GFA, de Boer WB. Surf. Interface Anal.1991: 17; 556.
[100] Prudon G, Dupuy JC, Bonneau M, Vandroux L, Dubois C, Gautier B, Vallard JP, Delmas J, Warren P, Dutartre D. Proc. of the SIMS X, Munster: Wiley; 1995, p. 687.
[101] G. Dong, C. Liangzhen, L. Rong, and A. T. S. Wee, Surf. Interface Anal. 32, 171 (2001).
[102] Sánchez-Almazán F, Napolitani E, Carnera A, Drigo AV, Isella G, von Känel H, Berti M. Appl. Surf. Sci. 2004: 231-232; 704.
[103] Jiang JX, Kim K, Lerma J, Corbett A, Sieloff D, Kottke M, Gregory R, Schauer S. Appl. Surf. Sci. 2006: 252; 7262.
[104] Ehrke HU, Mauel H, Mater. Sci. Semicond. Process. 2005: 8; 111.
[105] Dong G, Chao Q, Yizheng Z, Liangzhen C, Desse F, Schuhmacher M. Proc. SIMS XII, Amsterdam: Elsevier; 2000.
[106] Dowsett MG, Morris RJH, Hand M, Grigg AT, Walker D, Beanland R. Surf. Interface Anal. 2011: 43; 211.
[107] Morris RJH, Dowsett MG. J. Appl. Phys. 2009: 105; 114316.
[108] Zhu Z, Ronsheim P, Turansky A, Hatzistergos M, Madan A, Pinto T, Holta J, Reznicek A. Surf. Interface Anal. 2011: 43; 657.
[109] Py M, Barnes JP, Hartmann JM. Surf. Interface Anal. 2011: 43; 539.
[110] Prudon G, Gautier B, Dupuy JC, Dubois C, Bonneau M, Delmas J, Vallard JP, Bremond G, Brenier R. Thin Solid Films. 1997: 294; 54.
[111] Marseilhan D, Barnes JP, Fillot F, Hartmann JM, Holliger P. Appl. Surf. Sci. 2008: 255; 1412.
[112] P. Holliger, F. Laugier and J. C. Dupuy, Surf. Interface Anal. 34, 472 (2002).
[113] Gavelle M, Scheid E, Cristiano F, Armand C, Hartmann JM, Campidelli Y, Halimaoui A, Fazzini PF, Marcelot O. J. Appl. Phys. 2007:102; 074904.
[114] Saha B, Chakraborty P. Nucl. Instrum. Meth. B 2007: 258; 218.
[115] Sharma M, Sanyal MK, Mukhopadhyay M, Bera MK, Saha B, Chakraborty P. J. Appl. Phys. 2011:110; 102204.
[116] Saha B, Chakraborty P, Gnaser H, Sharma M, Sanyal MK. Appl. Phys. A 2012: 108; 671.