ANALYSIS OF NANOSTRUCTURES BY MEANS OF AUGER ELECTRON SPECTROSCOPY

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In modern nanotechnology analysis such methods are needed which are able to investigate extremely small volumes, thus surface sensitive techniques with a high spatial and depth resolution. Concerning the capability of high lateral and depth resolution, Auger electron spectroscopy (AES) is one of the outstanding analytical methods for nanotechnology. By field electron guns probe diameters below 10 nm are reached. Depth resolution of Auger electron spectroscopy, depending on the kinetic energy of the Auger electrons, is approximately 0.5 to 4 nm. Whereas large area AES has a detection limit of 0.1 at% it impairs for laterally highly resolved measurements. The article will give some examples for the application of Auger electron spectroscopy to nanostructures mostly in group III-nitride semiconductor technologies: (i) nanowires, consisting of Si and AlN with diameters of about 20 to 200 nm; these nanowires and nanorods have been grown by different technologies and some of them are contacted on both ends by FIB grown Pt contacts, (ii) nanoflowers,*ie* specially shaped up to 5 μm sized networks of AlN nanowires of about 20 nm in diameter, (iii) segregation structures of Si of 200 nm width, grown during PIMBE AlN epitaxy on Si substrate.

On the basis of these measurements the benefits and limits of Auger electron spectroscopy on nanostructures as well as some special effects which are characteristic especially for nanostructures, for instance resputtering and background signal contribution, are discussed.

K e y w o r d s: nanotechnology, Auger electron spectroscopy, nanowires, nanoflowers, segregation

1 INTRODUCTION

There are a lot of analytical methods using focused electron, ion or photon beams as well as mechanical tips as a probe for the excitation of a sample. Electrons, ions, neutrals or photons coming back from the sample as well as interaction forces between tip and sample surfaces can be measured. Each of these analytical methods is denoted by its special characteristics, possibilities, excellences, disadvantages and fields of application. This huge family of analysis methods can be classified into several groups: methods for chemical composition measurements and methods for the investigation of the structural, morphological and optical and electronic characteristics of the sample. Key characteristics of those methods are sensitivity, detection limit, elemental range, quantification and, as one of the most important features, the spatial and the depth resolution.

In modern nanotechnology analysis such methods are needed which are able to investigate extremely small volumes, thus surface sensitive techniques with a high spatial and depth resolution. Concerning the capability of high lateral and depth resolution Auger electron spectroscopy (AES) is one of the outstanding analytical methods for nanotechnology. In modern Auger spectrometers, equipped with a field electron gun, probe diameters below 10 nm are reached. Electron beams can be focused very well, whereas the focusing of ion beams and x-rays or visible light beams is much more complicated or impossible on the nanoscale. The depth resolution of Auger electron spectroscopy depends on the energy of the Auger electrons. But within the usual range from 50 eV to 2000 eV the attenuation length is approximately 0.5 to 4 nm. As a consequence most of the Auger signal comes from a thin sample surface layer with a thickness of some atomic layers. Whereas large area AES has a detection limit of 0.1 at% it impairs for laterally highly resolved measurements. With a detection limit of approximately 1 %, a spatial resolution of 10 nm and a depth resolution of 1 nm 50 atoms of one kind can be detected. No other method is able to reach the same detection limit, except for analytical cross-sectional transmission electron microscopy (XTEM) with very high preparation efforts and other constrictions.

With these properties AES can play an outstanding role for the analysis of nanostructures among other analysis methods like scanning transmission electron microscopy (STEM), photo emission electron microscopy (PEEM), small spot secondary ion mass spectroscopy (SIMS) and the scanning probe microscopy methods.

According to [1], problems are expected due to the complexity of nanostructures — due to the higher importance of surface phenomena compared to conventional microanalysis.

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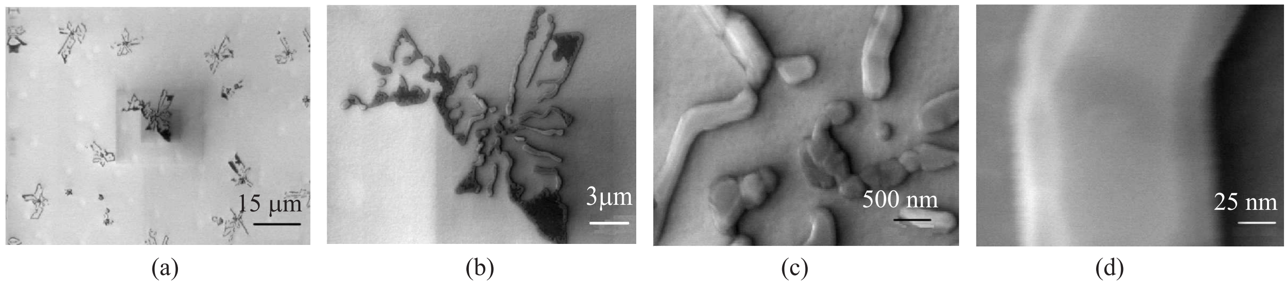

Fig. 1. Secondary electron microscopy (SEM) images of a Si segregation structure on AlN in different magnification

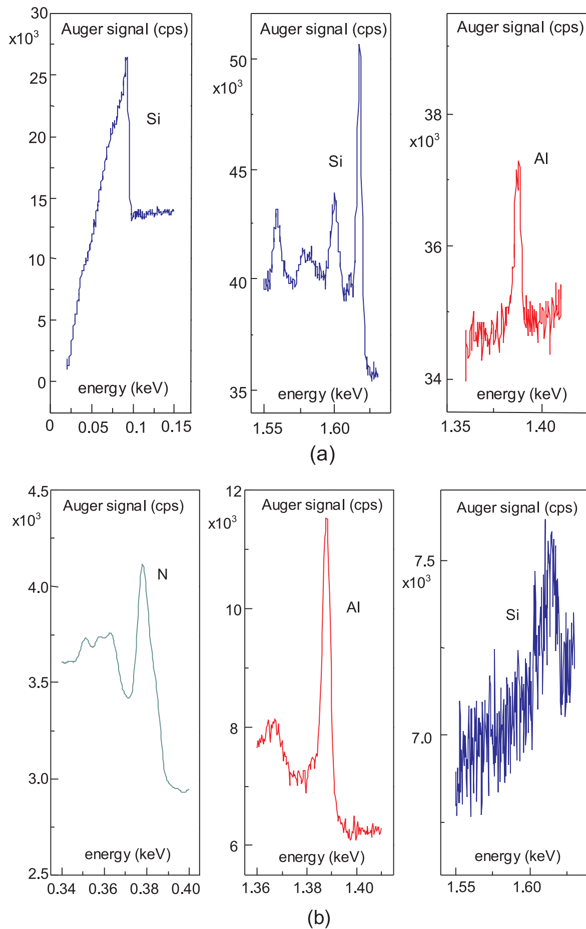

Fig. 2. AES spectra of Si, N and Al: (a) on the segregation structure and (b) besides the structure of the Al and Si images after sputter cleaning

2 EXPERIMENTAL

The following examples have been carried out by an Auger Microlab 350 by THERMO, equipped with a small spot electron gun with a field electron tip, an electron current of 0.1–100 nA. A spatial resolution of 7 nm for SEM images and 10 nm for Auger images can be achieved. Sputtering was carried out by a conventional Ar sputtering ion gun under 43°–74° with respect to the surface normal in the energy range of 0.5–5 keV.

A hemispherical energy analyzer of 0.03% energy resolution serves as an electron energy spectrometer. The energy resolution can be increased by retarding the electrons before passing through the analyzer. The measurements have been carried out in the direct mode $E\,N(E)$ with a constant retard ratio (CRR).

The nanostructure samples which are discussed in the paper have been grown by plasma induced molecular bam epitaxy (PI-MBE) in a BALZERS UMS500 and metallorganic chemical vapour deposition (MOCVD) in an AIX200 by Aixtron. Si and sapphire wafers have been used as substrates.

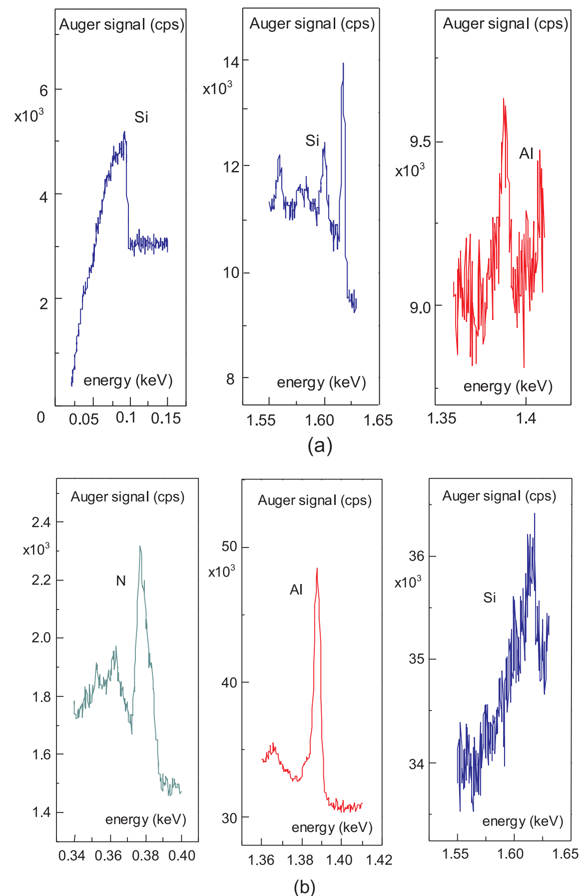

Fig. 3. AES spectra of Si, N and Al: (a) on the segregation structure and (b) besides the structure after sputter cleaning by Ar^{+} ion bombardment

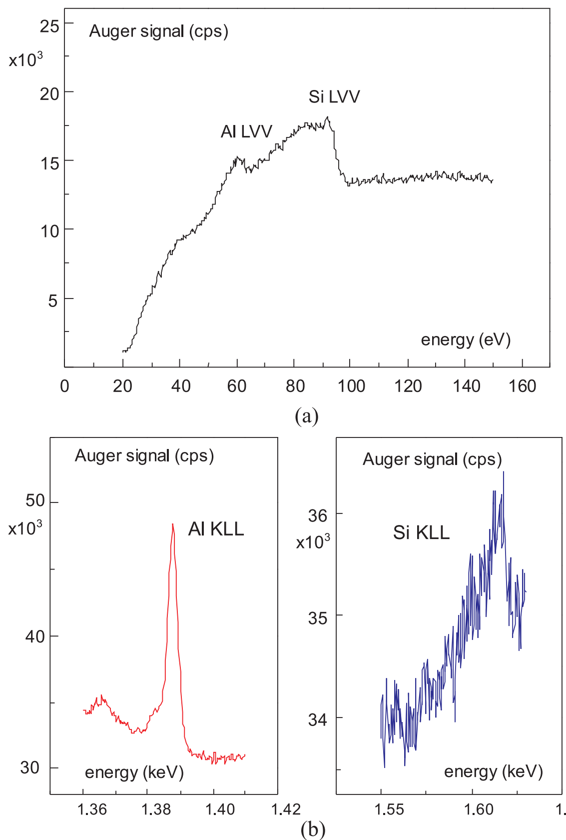

Fig. 4. AES spectra of Al and Si besides the structure after sputter cleaning, (a) LVV Auger peaks and (b) KLL Auger peaks

3 EXAMPLES

3.1 Example 1: Si segregating on epitaxial AlN

After the epitaxial growth of 50-200 nm thick Si doped AlN layers on Si substrates by plasma induced molecular beam epitaxy (PIMBE) segregation structures on the surface of the AlN layer could be detected [2]. These segregation structures consist of stripes with 0.1–1 μm width and up to some 10 μm length. Figure 1 shows the secondary electron microscopic image of the sample surface with one of the segregation structures in different magnifications.

It was assumed that silicon passes the AlN layer along grain boundaries from the substrate and segregates on the surface. AES spectra on and besides the segregation structure are shown in Fig. 2. One can see that in fact the segregation structure consists of silicon on the AlN layer. But traces of Al can be found on the Si structure and Si can be found on the AlN layer more surface more than the doping concentration. In order to decide, whether this is a surface effect or these are bulk concentrations, the sample has been sputter cleaned. The spectra of the sputter cleaned structure and layer are shown in Fig. 3. One can see that there is still Al on the segregation structure and Si on the AlN layer surface. If we measure the low energy LVV peaks and the high energy KLL peaks of Si and Al at the AlN surface (see Fig. 4), we can conclude that there is only a thin Si rich layer on the AlN, even after sputtering. This could be a result of sputter induced redeposition. To answer the question of the real concentration of Si within the AlN layer additional analysis is necessary which has been made by cross sectional TEM an electron energy loss spectroscopy, which is summarized in [3]. These measurements confirmed clearly the existence of Si segregation at dislocations within the AlN layer. With the good lateral resolution of the Auger spectrometer there is the possibility of acquiring scanning Auger maps (SAM) of these structures. Figure 5 shows the SEM images of the structure and Auger maps of Si and Al. The contrast can be enhanced after removing the surface adsorbates by sputter cleaning.

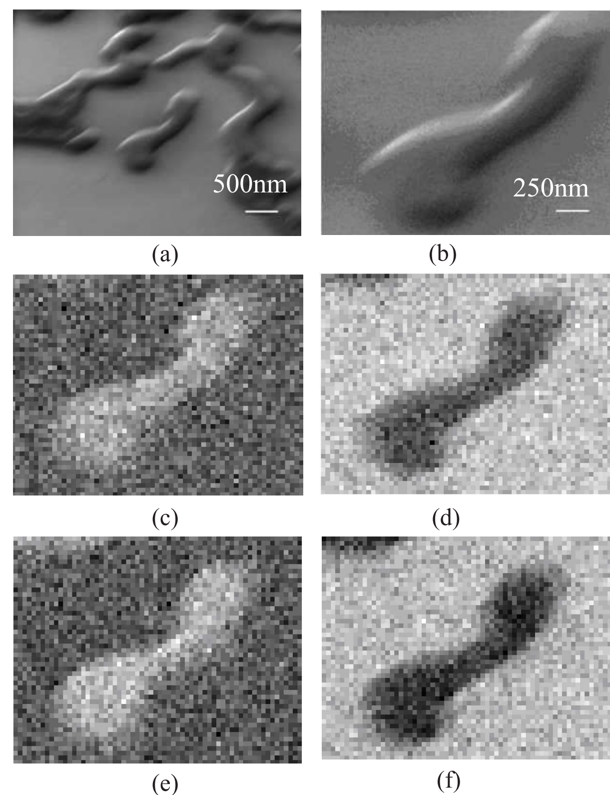

Fig. 5. SAM investigation of Si segregation: (a) and (b) SEM images in different magnification, (c) and (d) Al and Si SAM images before sputter cleaning and (e) and (f) with enhanced contrast of the Al and Si images after sputter cleaning.

3.2 Example 2: Pt contacted Si nanowires

On the SiO_2 surface of a Si/SiO_2 substrate Ti/Au metallisation pads have been created by means of magnetron sputtering. Afterwards, Si nanowires of approximately 150 nm diameter have been grown by low pressure chemical vapor deposition (LPCVD) on glass substrate and transferred onto the SiO_2 surface with the Ti/Au pad matrix. Focused ion beam technique (FIB) was applied to deposit Pt locally to connect both ends of the Si nanowires to the metallisation pads, in order to allow measuring the $I-U$ characteristics of these nanowires

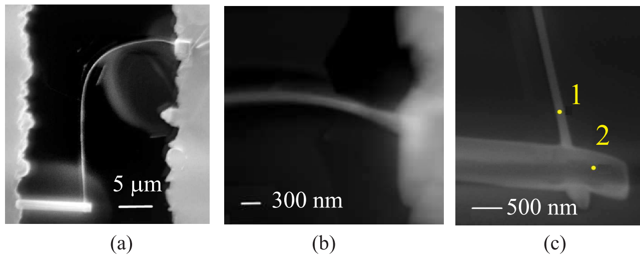

Fig. 6. SEM image of a contacted Si nanowire on SiO_2 surfaces: (a) nanowire and (b) (c) both contacts, in (c) the position of the AES measurements are indicated

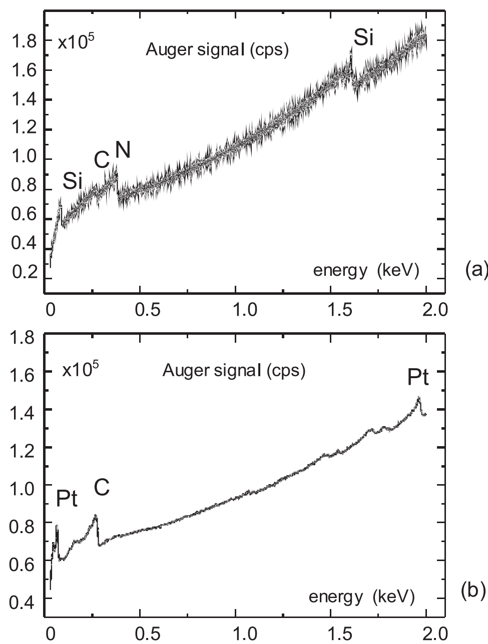

Fig. 7. AES spectra of (a) the Si nanowire according to position 1 in Fig. 6 (c) and (b) of the Pt metal connect according to position 2 in Fig. 6(c)

[4]. Figure 6 shows the SEM images of one nanowire and the contacts to the metallisation pads on both ends.

AES measurements were applied in order to measure the elemental composition of the nanowires and the composition of the FIB deposited Pt connects. AES results on two positions, indicated in Fig. 6 (c) show that the nanowire is consisting of Si which contains a high amount of nitrogen or SiN_x and that the metal connect which is made intentionally of Pt by FIB consists of Pt with a high C content (Fig. 7). After sputtering there is still a lot of N on the Si nanowire, indicating that the SiN_x mantle is relatively thick. After sputtering there is still the impurity of carbon in the Pt nanowire. Additionally we found that there is a heavy C contamination layer produced simultaneously during the Pt deposition by FIB all around the grown structure. The C amount is much higher and thicker than a common C contamination created by air.

3.3 Example 3: AlN nanoflowers

Under special conditions for the AlN growth on sapphire by metal organic chemical vapor deposition (MOCVD) special structures are developing, the so called 'nanoflowers' [5]. They consist of nanowires with diameters of about 20 nm. Figure 8 shows the SEM images of typical nanoflowers grown on a sapphire substrate in different magnifications. In Fig. 8 (c) one can see the nanowires which are the basis of these flowers.

With the high spatial resolution of AES it is possible to measure the composition of the nanowires either on one nanowire or on a conglomerate of nanowires.

Auger measurements shown in Fig. 9 reveal that the nanowires consist of AlN_x, but the surface of these wires is highly covered by C and O (not shown) which are adsorbates from the technological process or from the contamination by air before the Auger measurement. In such a case quantification of the measurement and conclusions on the stoichiometry of the AlN_x cannot be executed because the surface is contaminated and because of complete other backscattering conditions in nanowires compared to bulk or layer samples which must be used as standards.

3.4 Summary of examples

The three examples show the power of high spatially resolved Auger analysis on its application to nanostruc-

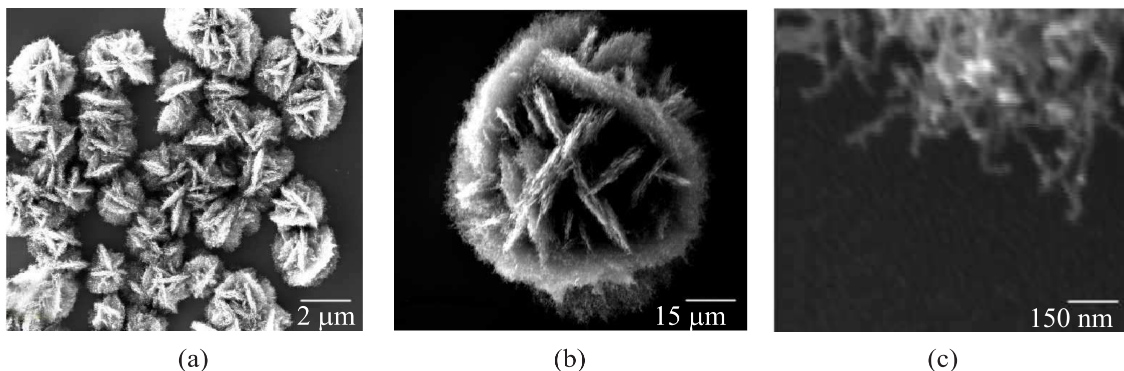

Fig. 8. SEM images of a 'nanoflower' in different magnifications

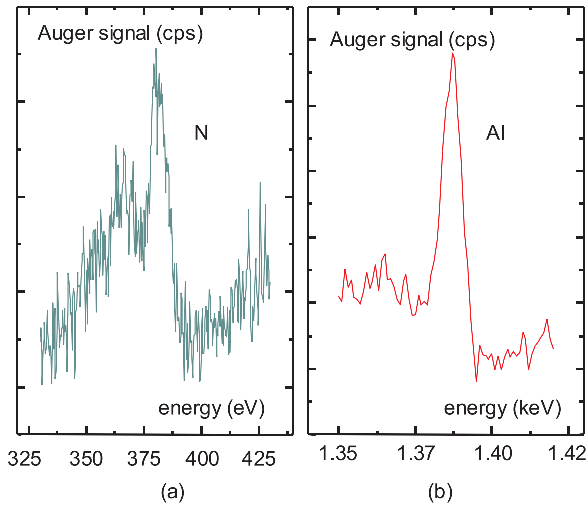

Fig. 9. Auger spectra of N KLL and Al KLL on a nanowire of a nanoflower

tures. But in all mentioned cases one can see that some artifacts could disturb the quality of the measurements, like sputtering induced redeposition, problems of quantification due to the backscattering behavior and the signal coming from the surrounding of a nanostructure by electron backscattering within the substrate.

4 GENERAL CONSIDERATIONS

In Auger analysis it is commonly known that

(i) the lower the primary energy of the electron gun, the worse is the spatial resolution,

(ii) the higher the beam current, the worse the spatial resolution,

(iii) but, the lower the primary excitation energy, the smaller is the area emitting Auger electrons due to backscattering.

Experiments have been carried out in order to explore this effect.

An InN particle of a size of approximately 1 μm on Si substrate has been measured with a relatively broad electron beam under excitation energies of 25 keV, 10 keV and 3 keV.

In and N signal comes from the particle itself, Si signal comes from the substrate due to electron backscattering and primary electron bombardment besides the particle.

Auger spectra for the three primary energies are shown in Fig. 10.

If we define the useful signal as a ratio of the signal of the particle (in our case In or N) to the signal of the substrate (Si), the useful signal can be evaluated of the measurement presented in Fig. 10. The useful signal In/Si and its dependence on the primary excitation energy is shown in Fig. 11. The insets show the corresponding SEM images and give an impression on the sharpness of the primary electron beam used for these measurements. It can be seen that for this measurement there is a maximum of the useful signal, *ie* an optimum of the primary electron excitation energy for acquiring the best measurement result. The energetic position of this maximum depends on

(i) the relation of the structure size and electron beam diameter,

(ii) the material and its backscattering behaviour and

(iii) the acquired Auger peak energies, because low energy Auger electrons are generated farther away from the structure by backscattering

(iv) the ionization cross-section of the core electron level of atom for primary electrons excitation energy.

It should be a fundamental aim for measuring nanostructures by AES to know about the optimal measuring conditions and to know about the possible artifacts. Additional measurements are necessary to clear this in a wide range of measuring parameters and materials.

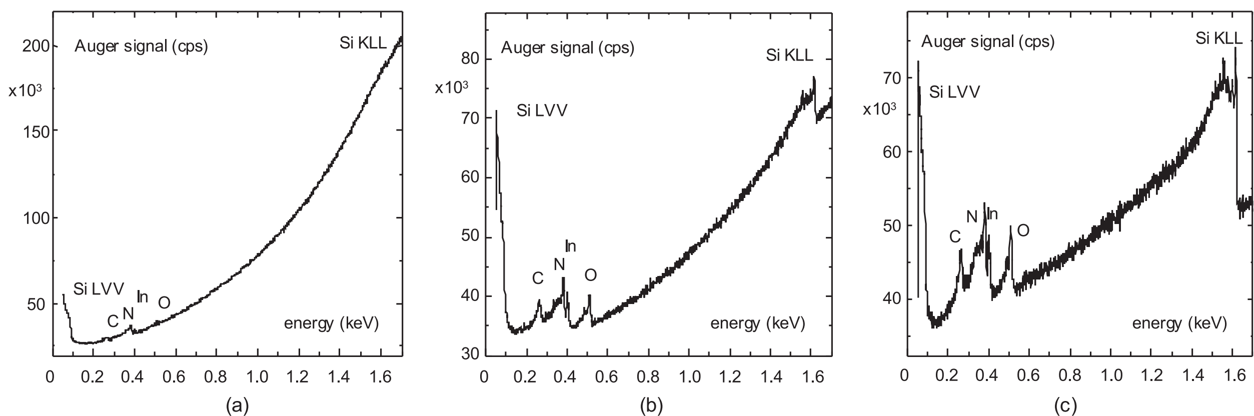

Fig. 10. Auger spectra of a InN particle on Si substrate with (a) 3 keV; (b) 10 keV and (c) 25 keV primary excitation energy

5 CONCLUSIONS

Three examples of Auger measurements on nanostructures are presented to document the capability of Auger electron spectroscopy as a surface sensitive technique with a brilliant spatial resolution. These properties enable this method to be one of the most promising surface analysis methods in nanotechnology research and development.

It has been shown that some artifacts can occur and it is important to know about them and regard them. It is of fundamental importance to know about optimal primary exciting electron energy and their dependence on the measured material and measuring conditions.

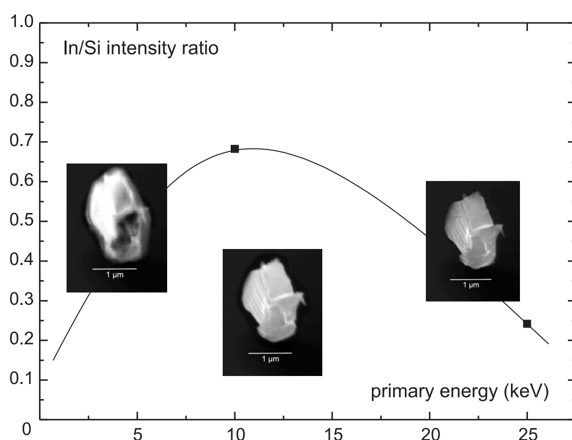

Fig. 11. Useful Auger signal In/Si of a InN nanoparticle on Si substrate and its dependence on the primary exciting energy, insets show the corresponding SEM images.

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