Surface Analysis by Auger Electron Spectroscopy

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We investigated the ternary II-VI compound semiconductors $Zn_{1-x}Mg_xTe$ $x \in [0, 1]$ by quantitative Auger Electron Spectroscopy. Emphasize was put on the behavior of the sensitivity factor s of the various constituents of the compound as a function of the composition of the ternary compounds. The sensitivity factors were calculated by a new formalism and showed a strong dependence on the compound composition. In the case of Te we found a change of the line shape and the appearance of Coster-Kronig transitions. Binary II-VI compounds like ZnSe, ZnTe, CdSe and CdTe were investigated with respect to their surface composition after reactive ion etching in CH_4/H_2 admixtures of different composition.

1. Introduction

The binary and ternary II-VI compound semiconductors are applicable to the production of blue light emitting diodes [1] – [3]. One of the main problems in these optoelectronic devices is the degradation, which is mainly caused by defects generated from strain and stress in the layers. A possibility to overcome that drawback is to fabricate lattice-matched multilayer structures. Since the lattice match is very sensitive to the composition of the compounds, an exact control during growth of the layers is indispensable. A method to control the composition is the Auger Electron Spectroscopy (AES). A main problem in quantitative AES (QAES) is that the sensitivity factors s of the constituents, which are equal to the probability of the occurrence of an Auger process [4] are only known for pure elements. Within this project we performed QAES on various compositions of $Zn_{1-x}Mg_xTe$ $x \in [0,1]$.

Parallel with the development of wide band gap II-VI blue-green diode lasers, the investigation of optical properties of quantum wires and dot structures has attained considerable interest [5] – [8]. An established method for the fabrication of lateral structures (e.g. quantum wires and dots) is the reactive ion etching (RIE) technique [9]. Most of the earlier studies of RIE on II-VI compounds used chlorine-containing gas mixtures [10]. In latter works a mixture of CH_4 and H_2 was used as etchant, which allows the fabrication of very small vertical structures with a minimal width of about 25 nm [11], [12]. In the literature a mixture between 1:6 and 1:8 for $CH_4:H_2$ ratio is reported to be an optimum etchant with respect to optical behavior of the fabricated nanostructures [5]. There are only few publications which are dealing with the chemical analysis of etched structures [13], [14].

We performed quantitative Auger electron spectroscopy (QAES) [15] analysis of ZnSe, ZnTe, CdSe and CdTe samples which were grown by molecular beam epitaxy (MBE) [16], and etched by RIE. In our analysis emphasize was given on the changes of the chemical composition of the etched samples due to the various ratios of $CH_4:H_2$ in the etchant not

only at the surface but also by depth profiling. In addition, the influence of oxygen as part of the etchant was investigated.

2. Results and Discussion

2.1. Sensitivity Factors

The sensitivity factors for Zn, Mg and Te as a function of the composition of the sample obtained with different primary electron energies were evaluated. A general trend could be seen that the sensitivity factors for all elements are increasing with increasing Mg content in the sample. Only the sensitivity factor of Te has a minimum in the range of x = 0.5. This is due to so-called Coster-Kronig transitions [16], which become dominant for samples with a composition around x = 0.5. The Auger spectra for $Zn_{1-x}Mg_xTe$ layers with different concentrations of Mg show beside the normal MNN Auger transitions also the MMN Coster-Kronig transitions. As a consequence the normal Auger transitions are decreased since the number of exciting primary electrons is constant in all the experiments.

2.2. Reactive Ion Etching

In the II-VI compounds ZnSe, ZnTe, CdSe and CdTe (i) the deviations from the stoichiometry, and the incorporation of (ii) oxygen and (iii) carbon were investigated as a function of the etching gas ratio in the RIE process.

(i) Down to a depth of about 20 Å the concentration of Zn and Se is lowered due to a large incorporation of carbon and some additional oxygen. The ratio of Zn to Se is nearly constant.

The lowest deviations from stoichiometry were found at $CH_4:H_2$ ratios of 1:6 and 1:7. Other $CH_4:H_2$ ratios showed large deviations from stoichiometry. For comparison, also as-grown samples were sputtered which showed no deviations from stoichiometry and indicate no effect due to preferential sputtering. Therefore we conclude, that deviations from stoichiometry which were investigated to a depth of 100 Å have their origin in the etching process.

(ii) The incorporation of oxygen into the samples could be clearly analyzed by QAES. In the case of Zn compounds the oxygen concentration is increasing with increasing hydrogen content in the etchant, whereas for the Cd compounds the oxygen content is decreasing. For a ratio of $CH_4:H_2$ of about 1:7 the incorporation of oxygen is low (between 1 and 2%) for all analyzed systems.

(iii) In contrast to oxygen, the carbon concentration decreases with sputter depth. The incorporation depth is between 20 and 80 Å. For Zn compounds, the C incorporation depth is lowest around a $CH_4:H_2$ ratio between 1:6 and 1:7, whereas for Cd compounds the depth is monotonically increasing with higher H_2 content. At a $CH_4:H_2$ ratio between 1:6 and 1:8, the incorporation depth is relatively low in all compounds.

3. Conclusion

The sensitivity factors for the constituent elements in the ternary II-VI compound $Zn_{1-x}Mg_xTe$ depend very strong on the composition of the compound.

For the investigated II-VI compounds (ZnSe, ZnTe, CdSe and CdTe) a relative small deviation from stoichiometry for a $CH_4:H_2$ etchant ratio around 1:7 is found as a common behavior. This is in agreement with literature, where an etchant with such a $CH_4:H_2$ ratio is used in order to give optimum optical behavior of the etched structures [5]. In addition, the incorporation of oxygen was detected over the whole investigated depth of 100 Å, whereas the carbon incorporation was limited to a depth between 20 and 80 Å.

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