Materials Science in Semiconductor Processing 82 (2018) 62–66

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

An X-ray photoelectron spectroscopy depth profile study on the InGeNi/(110) cleaved GaAs structure

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ARTICLE INFO

Keywords:
GaAs
XPS
Depth profile
Ohmic contact
Metal/semiconductor interface

ABSTRACT

InGeNi ohmic contacts on n-type semi-insulating GaAs(110) cleaved surfaces were fabricated. Cleaving semiconductor single crystal ensures the obtaining of semiconductor surfaces almost ideal in terms of chemical purity and stoichiometry. The chemical depth profile of metallic layer was investigated and revealed through multiple alternating steps of Ar^+ etchings and XPS (x-ray photoelectron spectroscopy) measurements. The metallic layers made of alloy of Ge, In and Ni (60 nm Ge, 60 nm In and 10 nm Ni), were obtained by thermal evaporation on cleaved surfaces in a high vacuum facility, followed by a thermal annealing at 430–450 °C for 5 min. Twelve etching sessions were required until the metal/semiconductor interface has been reached. A total of 14 etchings steps were performed during the experiment, a layer with a thickness of 140 nm being removed from the surface. The atomic concentrations of the constituent chemical elements were determined. In3d, In4d, Ga3d, Ga2p, As3d, As2p, $Ni2p^{3/2}$, Ge3d, O1s and C1s spectral lines were recorded and chemical bonds within the layer were analyzed from the fittings. The formation of $In_xGa_{1-x}As$ type compounds and of an intermediate semiconductor layer rich in Ge atoms at the interface was highlighted. X-ray detectors InGeNi/GaAs/Al and InGeNi/GaAs/Ti were fabricated with ohmic contacts based on this contacting scheme and Schottky interfaces prepared also by evaporation on cleaved edges. Electrical characteristics have been investigated and key diode parameters determined — ideality factor, Schottky barrier height, series resistance. Detection capabilities of these devices were studied in an x-rays flux, provided by a Co anode x-ray source.

1. Introduction

There are strong demands for x-ray detectors at room temperature based on semiconductor compounds in areas as medical imaging, astronomy, x-ray based spectroscopies, high energy physics. Semi-insulating GaAs (SI GaAs) compound is already known as a promising material in this field. Obtaining of Schottky devices on GaAs (SI) with good electrical properties is still a matter for improvement. A key aspect in this regard is the obtaining of ohmic contacts and also of Schottky contacts, a topic addressed in many laboratories. InGeNi contacting scheme uses the advantages of both methods of achieving low resistance ohmic contacts: the formation of a new heavily doped intermediate semiconductor layer at the interface and the formation of an intermediate layer which has a low barrier height at contact metals [1]. On usual GaAs, this type of contact is characterized by smooth surface, low contact resistance and good thermal stability, but on a semi-insulating semiconductor with very low carrier concentration, achieving these particularities is still an open problem.

In this metallization system the role of Ge is to diffuse in the semiconductor layer providing donors to GaAs. Also, the Ga atoms have a pronounced diffusion towards the surface, Ge atoms occupying the vacated sites. In this way the heavily doped intermediate layer is formed. In has the main role in creating a layer with low energy barrier. It is well known that at elevated temperatures (above 300 °C) $In_xGa_{1-x}As$ type compounds are formed and these have low energy barrier heights both at the GaAs and at the metal interface. The Fig. 1 shows the energy bandgap of $In_xGa_{1-x}As$ compound and the Schottky barrier height of $Au/In_xGa_{1-x}As$ structures calculated as in [2,3].

Ni plays the main role in keeping of good mechanical characteristics, thermal stability, surface smoothness. The contact morphology is however affected by the diffusion processes appeared during deposition and thermal annealing, by the chemical reactions in the layer width, by the presence of contaminants and various chemical compounds presents on the surface after etching treatment. In order to overcome some of the shortcomings imposed by a classical metallic deposition, in this work, a new way of obtaining InGeNi contacts is proposed – in-situ metallic

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https://doi.org/10.1016/j.mssp.2018.02.022
Received 28 June 2017; Received in revised form 9 February 2018; Accepted 16 February 2018
Available online 05 April 2018
1369-8001/

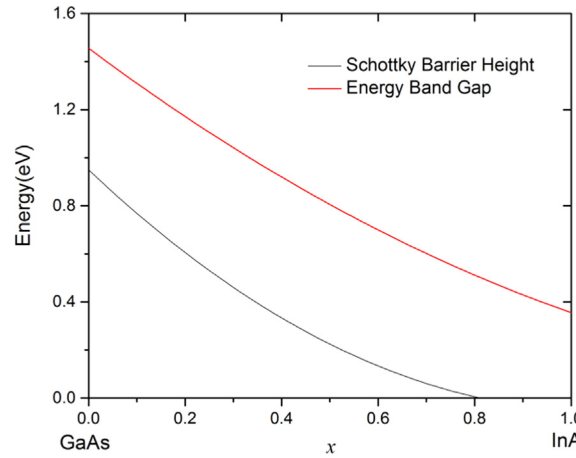

Fig. 1. Barrier height at Au/$In_xGa_{1-x}As$ interface and energy band gap of $In_xGa_{1-x}As$.

evaporation on very clean GaAs(SI) wafers cleaved in high vacuum right before starting the obtaining procedure. The research effort was expanded to a depth profile chemical analysis of ohmic contact layer and electrical characterization of a number of Schottky devices obtained by this method. Using XPS(x-ray photoelectron spectroscopy) measurements sessions combined with Ar^+ ion sputtering it is expected to obtain a clear image on chemical composition and interdiffusion processes in InGeNi ohmic layer and at metal/GaAs(SI) interface.

2. Experimental details

Schottky type structures have been prepared on n-GaAs(100) substrates by thermal evaporation from tungsten boat in high vacuum conditions. The GaAs(100) used was semi-insulating semiconductor with a resistivity greater than 10^7 Ωcm, provided by Wafer technology LTD. In, Ge and Ni were considered for the ohmic contact, while Al or Ti were considered for the Schottky type contact. All metals were provided by Sigma-Aldrich Chemie GmbH and were of high purity: 4 N for Ti and Ni and 5 N for Ge, In and Al. Prior each deposition process the GaAs wafer was cleaved in a custom device in high vacuum and the cleaved edge was aligned perpendicular to the direction of evaporation. The sequence of the operations was as follows. The GaAs wafer was mounted in the cleavage device and introduced in the evaporation chamber, the sample was cleaved and ohmic contacts were deposited. The sample was removed from the chamber and a thermal annealing was performed for 5 min and 430–450 °C in high vacuum. The obtaining of ohmic contacts was thus completed. The sample was mounted in the cleavage device with the opposite edge, then was reintroduced in the evaporation chamber; after cleavage, the Schottky contacts were deposited and the sample was again extracted. Another thermal annealing was followed – 370–400 °C and 5 min for Al type contact, 430–450 °C and 5 min in case of Ti type contact. The resulting detectors were 3 × 3 mm squares, with two deposited opposite edges. For ohmic contacts In, Ge and Ni were evaporated simultaneously from the same tungsten boat. In this way, a pre-alloying of the metal components was assured. The deposited quantities of each metal were calculated for a desired thickness of contact layer of 130 nm (60 nm In, 60 nm Ge and 10 nm Ni). The thickness of Ti or Al layers was 200 nm. Evaluation of electrical characteristics was performed on InGeNi/GaAs/Ti and InGeNi/GaAs/Al devices. For the depth profile study an InGeNi/GaAs device was considered.

The XPS measurements were carried out in a SPECS Multimethod Surface Analysis System, based on a PHOIBOS 150 hemispherical analyzer with an ultimate resolution of 0.44 eV (defined as FWHM(full width at half maximum) of recorded $Ag3d^{5/2}$ spectral line). The XPS spectrometer is not connected to the preparation chamber, therefore the atmospheric contamination of the samples could not be avoided during the transfer between the two. A monochromatic x-rays source XR50M source operated at 300 W, 15 kV produced the excitation radiation with an energy of 1486.6 eV (Al K_α) and a FWHM of 0.3 eV. An ultra-high vacuum of 10^{-9} mbar was maintained in the analysis chamber. The spectra corresponding to C1s, O1s, Ge3d, In3d, Ni2p, Ga3d, Ga2p, As3d, As2p, In4d, photoemission lines were recorded with a pass energy of 20 eV and a channel width of 0.05 eV.

For charge compensation a SPECS FG-40 flood gun device was used, providing an electron beam of 0.1 mA and 0.5 eV energy. Each set of XPS measurements was followed by a 5 min etching step carried out with an IQE11/35 ion gun operated at 3 kV accelerating voltage. The etching rate was estimated at 20 Å/minute, a number of 12 etching steps being made until the metal/semiconductor interface was revealed. The spectra fitting was made in SDP v2.3 (Spectral Data Processor) software using Voigt functions and Shirley baseline for background subtraction. Quantitative results were provided by the same software using the usual sensitivity factors. Electrical characterization of Schottky devices was performed in an assembly based on a Keythley 6517 A electrometer. The I-V characteristics were recorded in dark conditions and also in an x-ray flux provided by an x-ray source based on a BSV-22 X-Ray tube with Co anode, operated at 24 kV and 12 mA, 20 mA and 30 mA discharge currents.

3. Results

3.1. XPS depth profile measurements

The as-deposited InGeNi/GaAs sample was investigated before the depth profiling experiments commenced. The surface is covered with adventitious carbon and oxygen, but Ge, In, Ni, As and Ga are also present. The total quantity of O and C exceeds 60% of atoms of the surface. The XPS spectra shows a pronounced diffusion of Ga and this is beneficial since Ge atoms will find unoccupied vacancies in the GaAs bulk. Throughout the course of the experiment, carbon stops to occur in the deep layers of the metallic deposition, while oxygen concentration will follow a gradient, decreasing towards the interface. The oxygen is almost completely present as gallium oxide. Apparently, the presence of gallium in the layer induce oxygen diffusion and most likely it happens during the thermal annealing. On the non-etched surface, there are considerable amounts of oxides of other elements. As is found in a metallic state in a concentration of 38.7%, while in As_2O_3 and As_2O_5 the quantities are 39.1% and 22.2% respectively. Germanium from oxide totals no less than 40% of Ge amount, the rest being found in a metallic state. Indium is oxidized in a proportion of 30%. Only Ni remains as metal during the entire experiment. O1s spectrum indicate both metallic oxides but also C-O and –OH chemical bonds, molecular absorbed oxygen. After the first two etching sessions, only oxide associated with gallium remains visible in the spectra. The bulk metallic is composed from In, Ge, Ni, Ga and As. The relative concentration of this elements are presented in Fig. 2. The XPS intensity signal comes from a depth of approx. 10 nm, in which the calculation method assumes a chemical uniformity. Since 10 nm is also the thickness of the surface layer removed after each etching session, the values of the concentrations are not rigorously true.

Another aspect worth mentioning is that ion etching has different etch rates for different chemical elements. As is more easily to be removed than Ga and this affects the stoichiometry of the surface, even after the GaAs bulk is reached. In spite of these shortcomings affecting the calculation, the qualitative aspects of variation of concentrations are still valid. Close to the interface, photoelectrons are recorded from both GaAs and metal layers, but IMFP(inelastic mean free path) values in the two materials are slightly different. Therefore, the apparent loss of gallium at the interface is rather a calculation error due to the inhomogeneity of the analyzed layer. Indium has a stable behavior and as in the case of Ge, oxides disappear immediately after first etching step.