AIP | Conference Proceedings

The Influence of Surface Preparation on ZnDiffusion Processes in GaSb

T. Schlegl, O. V. Sulima, and A. W. Bett

Citation: AIP Conf. Proc. **738**, 396 (2004); doi: 10.1063/1.1841918

View online: http://dx.doi.org/10.1063/1.1841918

View Table of Contents: http://proceedings.aip.org/dbt/dbt.jsp?KEY=APCPCS&Volume=738&Issue=1

Published by the American Institute of Physics.

Related Articles

Manipulating InAs nanowires with submicrometer precision
Rev. Sci. Instrum. 82, 113705 (2011)

Local domain sensing with nanostructured tunneling anisotropic magneto resistance probes
Appl. Phys. Lett. 99, 202504 (2011)

Raman and photoluminescence characterization of focused ion beam patterned InGaN/GaN multi-quantum-wells nanopillar array
J. Appl. Phys. 110, 093111 (2011)

Transmission electron microscopy study of GaInNAs(Sb) thin films grown by atomic hydrogen-assisted molecular beam epitaxy
Appl. Phys. Lett. 99, 191907 (2011)

Adatom kinetics on nonpolar InN surfaces: Implications for one-dimensional nanostructures growth
Appl. Phys. Lett. 99, 193106 (2011)

Additional information on AIP Conf. Proc.

Journal Homepage: http://proceedings.aip.org/

Journal Information: http://proceedings.aip.org/about/about_the_proceedings

Top downloads: http://proceedings.aip.org/dbt/most_downloaded.jsp?KEY=APCPCS

Information for Authors: http://proceedings.aip.org/authors/information_for_authors

ADVERTISEMENT

Submit Now

Explore AIP's new open-access journal

• Article-level metrics now available

• Join the conversation! Rate & comment on articles

Downloaded 18 Nov 2011 to 141.213.172.89. Redistribution subject to AIP license or copyright; see http://proceedings.aip.org/about/rights_permissions

HTML ABSTRACT + LINKS

The Influence of Surface Preparation on Zn-Diffusion Processes in GaSb

T. Schlegl[1,2*], O. V. Sulima[1**], A.W. Bett[1]

[1] *Fraunhofer Institute for Solar Energy Systems ISE, Heidenhofstrasse 2, 79110 Freiburg, Germany*
[2] *Freiburger Materialforschungszentrum, Stefan-Meier-Strasse 21, 79104 Freiburg, Germany*
[*] *corresponding author: tschlegl@ise.fraunhofer.de*

** Current address; GE Energy (USA) LLC, 231 Lake Drive, Newark, Delaware 19702, USA

Abstract. Zinc diffusion is an established process for doping III-V semiconductors. The experimentally observed kink-and-tail Zn doping profile in GaSb can be explained by two different diffusion mechanisms. However, the reproducibility of the doping profile strongly depends on the treatment of the wafers before the diffusion process. Significant changes in the doping profile have been observed even under small variation in surface preparation. It is found that surface oxides strongly influence Zn profiles. Oxides change the solubility of Zn in GaSb and appear to influence the diffusion mechanism. Different cleaning procedures also alter the profile. This can be explained by defects resulting from cleaning residues. Various surface preparation methods and their resulting doping profiles are discussed.

INTRODUCTION

Gallium antimonide (GaSb) is of increasing interest for photovoltaic and thermophotovoltaic applications. To establish GaSb technology for a wide range of applications, the large-scale production of GaSb devices has to be highly reproducible, simple and safe. The technique of Zn vapour diffusion fulfils these requirements and has become a mature technology for doping of various Sb-based compound semiconductors [1].

The kink-and-tail doping profile achievable with such a technique makes Zn attractive as a p-dopant, because it provides flexibility for device designers. On the other hand, it is also a sign of a complex and non-ideal diffusion process, which requires a comprehensive study.

By Boltzmann-Matano analysis it has been shown [2] that the non-ideal diffusion in GaAs depends on the Zn concentration. Very often step-like Zn diffusion profiles can be observed. It is widely accepted that this phenomenon can be explained by an interstitial-substitutional diffusion model [2-6]. The diffusion mechanism governing Zn in GaSb is considered to be similar to that of GaAs [2].

Downloaded 18 Nov 2011 to 141.213.172.89. Redistribution subject to AIP license or copyright; see http://proceedings.aip.org/about/rights_permissions

In this model most of the dissolved Zn is present substitutionally, occupying sites on the Ga sublattice as a shallow acceptor (Zn^{-}_{Ga}) [7]. Interstitial Zn is considered to be an ionised donor (Zn^{+}_{i}). Its solubility in GaSb is several orders of magnitude smaller than that of the substitutional Zn^{-}_{Ga} , hence

$$[Zn^{+}_{i}] << [Zn^{-}_{Ga}] = p \approx [Zn]. \quad (1)$$

But due to its much higher diffusivity Zn^{-}_{Ga} dominates the diffusion process. Square brackets denote concentration. Immobile Zn^{-}_{Ga} atoms can become $Zn^{+}_{i,}$ which then diffuse in an ideal manner before moving back onto substitutional sites. This interchange of Zn^{-}_{Ga} and Zn^{+}_{i} atoms can be described by two simple mechanisms, the vacancy mechanism [8],

$$Zn^{+}_{i} + V_{Ga} \leftrightarrow Zn^{-}_{Ga} + 2h^{+} \quad (2)$$

and the kick-out-mechanism [4]:

$$Zn^{+}_{i} \leftrightarrow Zn^{-}_{Ga} + Ga_{i} + 2h^{+} \quad (3)$$

V_{Ga} and Ga_{i} represent a gallium vacancy and an interstitial gallium atom respectively. Interstitial Zn (Zn^{+}_{i}) is assumed to be a singly ionised donor. The exchange of Zn^{+}_{i} and Zn^{-}_{Ga} requires in both mechanisms two holes (h^{+}), hence by mass action each reaction depends on $[Zn]^{2}$. Therefore, the probability of substitutional Zn becoming interstitial also depends on the square of the zinc concentration [3].

Both mechanisms (2) and (3) would not work without defects in the crystal. An increase in the number of defects should therefore enhance the diffusion process. Nichols et al. [9] showed that the kink-and-tail Zn diffusion profiles in GaSb correlate with the presence of a dislocation network behind the diffusion front for Zn surface concentrations exceeding 10^{20} cm^{-3}. Defect-free box-shape diffusion profiles were observed for Zn surface concentration below 10^{20} cm^{-3} [9].

Defects are always present in the crystal and can be additionally provided by the surface. As a consequence, the treatment of the surface is expected to significantly influence the resulting doping profile. The exact shape of the profile depends on the treatment of the wafer before the diffusion. This work demonstrates the influences of surface preparation and explains its effect on the diffusion process of Zn in GaSb.

EXPERIMENTAL

For forming p-n junctions in n(Te)-doped GaSb the pseudo-closed box method is used. Doping by diffusion out of the gas phase is inexpensive and simple. This is mirrored in the equipment that is used for the experiments, consisting of three main parts: a quartz tube, a furnace and a graphite crucible. The graphite crucible inside the tube can hold up to three 6 cm^{2} wafers. The crucible also contains Zn for the wafer

Downloaded 18 Nov 2011 to 141.213.172.89. Redistribution subject to AIP license or copyright; see http://proceedings.aip.org/about/rights_permissions

doping and antimony to maintain a relatively high Sb vapour pressure to avoid Sb desorption from the GaSb surface [10]. It is important because the Zn diffusivity depends on group III vacancies [7]. Sb desorption leads to a random generation of vacancies and thus results in irreproducible diffusion profiles.

The quartz tube is evacuated before each diffusion process, filled with hydrogen and flushed during the diffusion at low hydrogen flow rate. The evacuation of the quartz tube and the hydrogen overpressure prevent growth of a surface oxide on the GaSb surface. The furnace design ensures constant temperature within the graphite crucible. All diffusions took place for four hours at 495°C. To guarantee the fastest possible ramping up of the crucible temperature the furnace is first heated up to 540°C. The diffusion process is started by moving the furnace over the crucible while lowering the set-point of the temperature controller to 495°C. The diffusion ends when the furnace is removed.

Te doped n-type GaSb wafers with a concentration of 2-4 x 10^{17} cm^{-3} were used. In our equipment GaSb samples of a maximum size of 25 x 25 mm can be processed. Before dicing appropriate pieces out of 2 inch wafers, the wafers are protected by an anodic oxide and a lacquer layer. The lacquer is removed by an acetone cascade and isopropanol. In a standard cleaning procedure the anodic oxide is removed before diffusion by hydrochloric acid (HCl). It is slowly diluted by deionised water to a concentration of about 1:15. The wafers are then dried with nitrogen (N_2) and transferred to the crucible as soon as possible. The time between the removal of the wafers from the diluted HCl and the evacuation of the quartz tube, during which time native oxide can form, was usually around seven minutes unless mentioned specifically.

Zn concentration was measured by secondary ion mass spectroscopy (SIMS) by RTG Microanalyse GmbH, using IMS CAMECA. Cs^+ ions (energy of 5.5 keV) sputter GaSb and form ZnCs clusters which are then detected. The Zn concentration detected directly under the surface is considered to be too low since the stoichiometric balance of forming and destroying clusters under Cs bombardment is reached only after a few nanometers. Hence for pure GaSb an increase of the Zn concentration signal is always observed within the first 20 nm from the surface.

A peak of the SIMS signal of Zn concentration at the surface is a sign for incorporation of O atoms into the crystal. O atoms result in an elevated probability of ionisation and hence in an elevated SIMS signal. The errors in measurements are about 10 % in concentration and 2 % in depth of the GaSb crystal and a little higher in the depth when oxides are measured. Both a peak and a gap in the Zn concentration signal are artifacts of the measurement, but can indicate the presence or absence of an oxide respectively.

The influence of the pre-diffusion treatment of GaSb on the doping profile was investigated by the variation of three parameters: (i) thickness of the GaSb native and anodic oxide, (ii) last step in the preparation procedure, and (iii) cleaning procedure itself.

Downloaded 18 Nov 2011 to 141.213.172.89. Redistribution subject to AIP license or copyright; see http://proceedings.aip.org/about/rights_permissions

RESULTS AND DISCUSSION

In a first experiment we varied the time, within which a freshly prepared surface was exposed to the atmosphere before being placed in the quartz tube for Zn diffusion. All the GaSb samples were cleaned in the identical manner. Figure 1 shows that a small variation in the time between the cleaning process and the diffusion vacuum causes a significant change in the post-diffusion profile of the Zn concentration. The sample, which was exposed to atmosphere beforehand for 20 minutes, exhibits a much deeper doping profile, i.e. a much deeper first plateau but a shorter second one than the sample, which was placed in the evacuated tube after only three minutes.

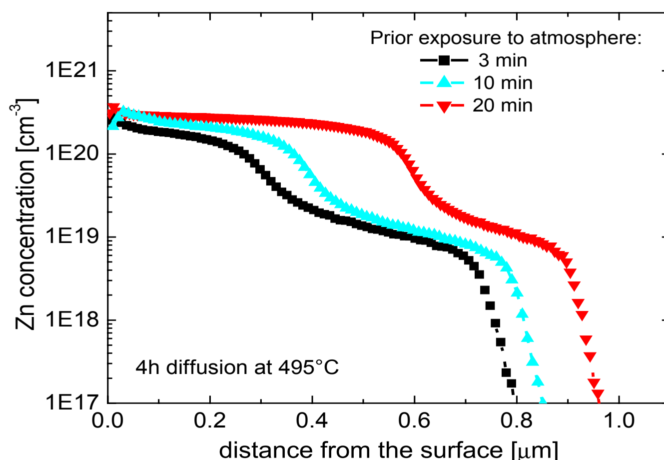

FIGURE 1. Zn-diffusion kink-and-tail doping profiles illustrating their sensitivity to surface preparation. The cleaning process for the samples was identical, but the samples were exposed to atmosphere for different time periods prior to the diffusion process.

In order to understand these experimental results, the process of native oxidation was investigated. The GaSb oxidation process is rapid enough for a native oxide to grow significantly in only a few minutes. It has been observed that the amount of native oxide of GaSb increases in air linearly on a logarithmic time scale, as shown in Figure 2. The oxide layer on a GaSb sample was removed by the described standard cleaning procedure. After drying with N_2 the native oxide layer thickness was determined by an ellipsometer measurement.

Downloaded 18 Nov 2011 to 141.213.172.89. Redistribution subject to AIP license or copyright; see http://proceedings.aip.org/about/rights_permissions

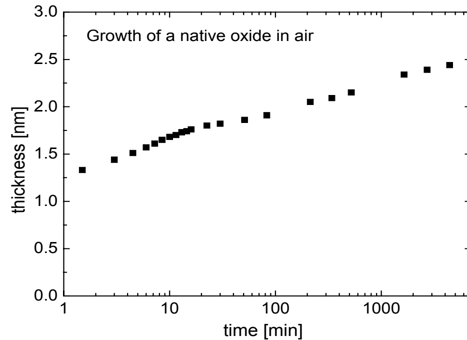

FIGURE 2. Time dependence of the growth of GaSb native oxide.

Although the increase in the thickness of the oxide is in total rather small, it clearly has a strong influence on the diffusion of Zn as the different doping profiles show. Since the doping profile strongly changes with the uncontrollable formation of a native oxide, a well-defined, artificial anodic oxide could result in a better reproducibility of the profile. The process of forming the anodic layer is described in [10]. Diffusion processes were conducted into anodic oxides with a thickness of 12, 23 and 104 nm. Figure 3 shows the comparison of diffusion profiles in anodically oxidized samples and in a sample with a standard cleaning process. For the SIMS measurements the anodic oxide layers were not removed.

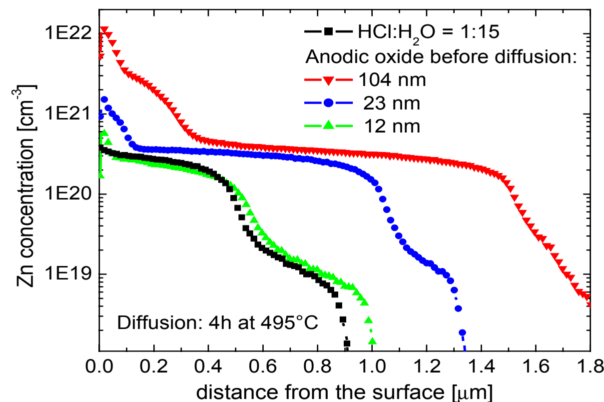

FIGURE 3. Anodic oxides enhance the Zn diffusion process in GaSb.

The peak of the SIMS measurement of the oxides directly under the surface corresponds well with oxide thickness. The measurement of the 104 nm oxide clearly shows that the solubility of Zn in an oxide is increased compared to bulk GaSb.

Downloaded 18 Nov 2011 to 141.213.172.89. Redistribution subject to AIP license or copyright; see http://proceedings.aip.org/about/rights_permissions

Oxides appear to enhance the diffusion of Zn into GaSb and to increase the solubility of Zn in the crystal. The reason for this could be defects of the crystal resulting from the oxide. Oxygen atoms could diffuse into the GaSb bulk. Since the solubility of Zn is higher in the oxide than in the crystal this might explain the elevated solubility in the bulk.

In order to obtain a kink-and-tail profile, surface concentrations exceeding $10^{20}cm^{-3}$ are necessary [9]. Higher concentrations i.e. an increased solubility of Zn in oxides might enhance the diffusion process responsible for the kink. Hence Zn diffusion with oxides yields to a deeper doping profile. This could explain the fact that oxides influence the ratio of the two plateaus as can be seen in Figures 1 and 3. The second plateau becomes shorter with increasing oxide thickness until it nearly vanishes at the oxide thickness of 104 nm.

When a Zn diffused profile is used as an emitter of a photovoltaic cell [11], the highly doped first plateau is considered to be electrically dead and is usually etched away. Keeping this part as thin as possible by preventing the formation of a native oxide could facilitate the production and improve reproducibility of these PV cells. Therefore, different methods of preventing exposure of the samples to atmosphere through using of an oxygen-free environment (ethanol, nitrogen and isopropanol) were examined. The time required for the formation of a native oxide was much less than a minute; therefore the samples were taken from their environments and put directly into the quartz tube, which was immediately evacuated.

It was found that these procedures influence the diffusion profiles in different ways, as shown in Figure 4. Considering the above results it was expected that these experiments, due to a thinner native oxide, would yield shallower diffusion profiles than those obtained from the standard surface preparation. Surprisingly, in the cases of ethanol and nitrogen the diffusion profiles were deeper.

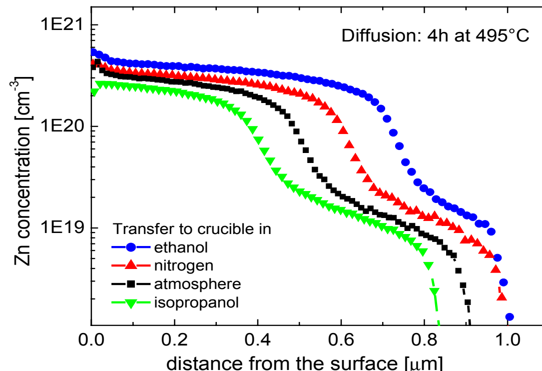

FIGURE 4. The influence of the pre-vacuum environment during the transfer to the curcible on the diffusion profile.

In both cases however there is a peak in Zn concentration directly under the surface signaling that the formation of a native oxide was not prevented effectively. The

Downloaded 18 Nov 2011 to 141.213.172.89. Redistribution subject to AIP license or copyright; see http://proceedings.aip.org/about/rights_permissions

reasons therefore are to be investigated in further experiments. The use of isopropanol however prevents the formation of a native oxide as the gap directly under the surface indicates, yielding to improved doping profile.

In a final experiment the influence of different acids for oxide removal was investigated. Four wafer pieces were treated with HCl by four different processes: the standard surface preparation as described above, pure HCl, HCl gradually replaced by H_2O and HCl gradually replaced by isopropanol. A fifth piece was treated with diluted HF. The removing of the etchant was always performed by nitrogen. After that the wafers were exposed to atmosphere, between 16 and 19 minutes for the samples cleaned by HCl and 6 minutes for the sample cleaned by HF.

Figure 5 compares the resulting doping profiles. H_2O forms an oxide which influences the diffusion profile in a similar manner to anodic oxides, as described above. All treatments by HCl do not hinder the growth of a native oxide. Only the treatment with diluted HF seems to impede the growth of a native oxide, which can be asserted by the resulting shorter diffusion depth and the lack of a peak at the surface.

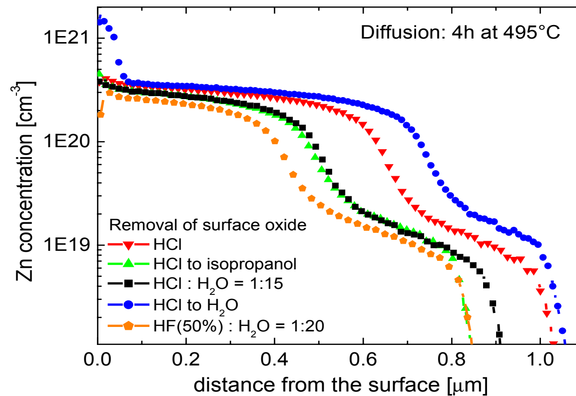

FIGURE 5. Different methods of surface cleaning also vary the growth of a native oxide.

CONCLUSIONS

The influence of different surface preparation methods on the Zn diffusion process in GaSb was studied for the first time. It is shown that even small variations in wafer treatment strongly influence the doping profile. Oxides are found to increase the highly doped part of the diffusion profiles. In order to improve reproducibility of the Zn diffusion process and to stabilize the GaSb surface a thin precisely controllable anodic oxidation of 10 nm is suggested.

Downloaded 18 Nov 2011 to 141.213.172.89. Redistribution subject to AIP license or copyright; see http://proceedings.aip.org/about/rights_permissions

ACKNOWLEDGEMENTS

The financial support of the Deutsche Bundesstiftung Umwelt (DBU; Osnabrück, Germany) to T. Schlegl is gratefully acknowledged. We acknowledge the financial support by the European Commission within the project FULLSPECTRUM Contract number (SES6-CT-2003-502620). The authors are responsible for the content of this work.

REFERENCES

[1] O. V. Sulima, A. W. Bett, G. M. Mauk, B. Y. Ber, and P. S. Dutta, *Diffusion of Zn in TPV materials: GaSb, InGaSb, InGaAsSb and InAsSbP*, In Proc. 5th Conference on Thermophotovoltaic Generation of Electricity, ed. by. G. G. T.J. Coutts, J. Luther (American Institute of Physics 2002) S. 402-413

[2] B. Tuck, *Mechanisms of atomic diffusion in the III-V semiconductors*, Journal of Physics D (Applied Physics) **18** (1985) 557-584

[3] G. J. Conibeer, A. F. W. Willoughby, C. M. Hardingham, and V. K. M. Sharma, *Zinc diffusion in tellurium doped gallium antimonide*, In Proc. Materials for Optoelectronics (Elsevier 1995) S. 21-25

[4] U. Gösele and F. Morehead, *Diffusion of Zinc in gallium arsenide: A new model*, J. Appl. Phys. **52** (1981) 4617-4619

[5] S. Reynolds, D. W. Vook, and J. F. Gibbons, *Open-tube Zn diffusion in GaAs using diethylzinc and trimethylarsenic: experiment and model*, Journal of Applied Physics **63** (1988) 1052-1059

[6] K. B. Kahen, *Model for the diffusion of zinc in gallium arsenide*, Applied Physics Letters **55** (1989) 2117-2119

[7] B. Tuck, *Atomic Diffusion in III-V Semiconductors* (IOP, Bristol, 1988)

[8] F. C. Frank and D. Turnbull, *Mechanism of diffusion of copper in germanium*, Phys. Rev. **104** (1956) 617-618

[9] S. P. Nicols, H. Bracht, M. Benamara, Z. Liliental-Weber, and E. E. Haller, *Mechanism of zinc diffusion in gallium antimonide*, Physica B (2001) 854-857

[10] O. V. Sulima, A. W. Bett, and J. Wagner, *Anodic Oxidation of GaSb in Acid-Glycol-Water Electrolytes*, Journal of Electrochemical Society **147** (2000) 1910-1914

[11] O. V. Sulima and A. W. Bett, *Fabrication and Simulation of GaSb Thermophotovoltaic Cells*, Sol. Energy Mater. Sol. Cells **66** (2001) 533-540

Downloaded 18 Nov 2011 to 141.213.172.89. Redistribution subject to AIP license or copyright; see http://proceedings.aip.org/about/rights_permissions