Sulfur Passivation of GaAsSb alloy layer Surfaces: Comparison of Ammonium Sulfide and Disulfur Dichloride Solutions

Shouzhu Niu

National Key Laboratory of High-Power Semiconductor Lasers
Changchun University of Science and Technology
Changchun , China
nszcc@outlook.com

Dan Fang*

National Key Laboratory of High-Power Semiconductor Lasers
Changchun University of Science and Technology
Changchun , China
fangdan19822011@163.com

Jilong Tang

National Key Laboratory of High-Power Semiconductor Lasers
Changchun University of Science and Technology
Changchun , China
jilong_tangcust@163.com

Fang Fang

Nanchang University
Nanchang , China
fang_fang0131@126.com

Xuan Fang

National Key Laboratory of High-Power Semiconductor Lasers
Changchun University of Science and Technology
Changchun , China
fangxuan110@hotmail.com

Jinhua Li

National Key Laboratory of High-Power Semiconductor Lasers
Changchun University of Science and Technology
Changchun , China
lijinhua2000@hotmail.com

Xiaohua Wang

National Key Laboratory of High-Power Semiconductor Lasers
Changchun University of Science and Technology
Changchun , China
biewang2001@126.com

Zhipeng Wei

National Key Laboratory of High-Power Semiconductor Lasers
Changchun University of Science and Technology
Changchun , China
zhipengwei@gamil.com

Abstract—In this paper, (NH4)2S and S2Cl2 are used as passivating agent for the sulphuration treatment to GaAs0.03Sb0.97. The effect of surface passivation of GaAs0.03Sb0.97 by (NH4)2S and S2Cl2 treatment is investigated by using photoluminescence (PL), Atomic Force Microscope (AFM). Compared with the pristine sample, the PL intensities of GaAs0.03Sb0.97 that treated by (NH4)2S and S2Cl2 both are increased significantly. The PL intensity is strongly dependent on passivation time. For the 10s S2Cl2-treated sample, the peak intensity is about 1.4 times larger than 20 min (NH4)2S-treated sample. Meanwhile, AFM images indicate that the roughness of the S2Cl2 treated sample is smaller than the (NH4)2S treated sample. Thus, S2Cl2 passivation is an effective method in improving the optical properties of GaAs0.03Sb0.97 material.

Keywords-component; GaAsSb; Passivation; (NH4)2S; S2Cl2; Photoluminescence

I. Introduction

Group III–V semiconductors are widely investigated for high speed electronic devices, micro- and optoeletronic devices [1,2]. Mixed group-V compound GaAsSb alloy material has attracted many attentions because of GaAsSb can emit light in the infrared regime. Therefore, GaAsSb alloy material can be used in optical communication applications, such as lasers [3,4].

However, the full potential of III-V-based devices cannot be realized because of their surface properties. The surface of III–V semiconductor oxidizes under atmospheric conditions forming a several-nanometer thick of oxide layer [5]. That will giving rise to unwanted conduction paths parallel to the interface and high surface state density [6]. It leads to the generation of electronic states in Fermi level pinning on semiconductor surface. Fermi level pinning detrimentally affects the performance

of semiconductor devices by creating Schottky metal contacts, carrier depletion, and electron–hole recombination at the surface states [7]. The high surface state densities, high surface recombination which can deeply hindered the development of GaAsSb-based devices. Therefore, it is important to control the electronic structure and surface state density to optimize the performance and the reliability of GaAsSb-based devices.

To reduce the detrimental effects of surface states on the optical and electrical properties of semiconductors, surface passivation can be applied to reduce the density of surface states. So far, many different passivation techniques have been used to overcome these surface leakages. Dielectric material deposition, sulfur passivation, over growth with wide band gap materials, and polymer film coating techniques can be listed as successful methods for passivation[8-11]. Sulfur containing solutions satisfies dangling bonds and cleans the conductive native oxides by replacing the oxygen atoms with sulfur atoms. Recent research indicates that the sulfur treatments can reduce the surface Fermi-level pinning, the surface recombination velocity (SRV) interface state density in metal–insulator–semiconductor (MIS) and increase the intensity of photoluminescence [12-15]. Therefore, the effect of sulfur passivation of the GaAsSb materials is deserves to further study.

In this paper, grow GaAsSb alloy layer by MBE and present a study of the efficacy of sulfur passivation treatment of the GaAsSb surface. The $(NH_4)_2S$ and S_2Cl_2 solution are used to passivation and compared the results of the two methods. X-ray diffraction spectrum indicated that the crystalline quality of $GaAs_xSb_{1-x}$ (x=0.03) substrate is satisfactory. Comparing to the untreated $GaAs_{0.03}Sb_{0.97}$, the PL intensity of the $GaAs_{0.03}Sb_{0.97}$ passivated by $(NH_4)_2S$ and S_2Cl_2 both are increased significantly. However, S_2Cl_2 treatments have a better effect than $(NH_4)_2S$ treatments. Meanwhile, AFM images indicated that the roughness of the S_2Cl_2 treated sample is better than the $(NH_4)_2S$ treated sample.

II. EXPERIMENTAL DETAILS

The $GaAs_xSb_{1-x}$ (x=0.03) alloy described here is grown by DCA P600 solid-source molecular beam epitaxy (MBE) machine equipped with valved As and Sb crackers. The 350μm thick semi-insulating GaSb substrate to be outgassed in vacuum at 390℃ for several hours. The holder is then loaded into the growth chamber, and the oxide layer is desorbed under Sb2 flux by increasing the substrate temperature to 650℃. After 15 min, the temperature dropped to 550℃. Then, the 1 μ m $GaAs_xSb_{1-x}$ alloy layer of is grown at 550℃.

The as-grown $GaAs_xSb_{1-x}$ is cleaved into 5 pieces and they are cleaned by acetone, ethanol and deionized water using ultrasonication for 5 minutes sequentially. Subsequently, the substrates are immersed in the HCl solution for 1 min to remove the native oxides. The samples are rinsed again in DI water and finally blown dry with compressed N2 gas. One sample is a reference sample without sulfur treatment. Two samples are soaked in 8% $(NH_4)_2S$ solution for 10 min and 20 min at 60℃. The last two samples are immersed in solution containing S_2Cl_2 and CCl4 in a volume ratio 1:3 for 5s and 10s at room

temperature.Then, all the samples are rinsed using DI water and finally blown dry with compressed N2 gas.

All samples are investigated by photoluminescence spectroscopy mapping (PL, RPM 2000) and atomic force microscope (AFM,). The crystal structure of the GaAsSb is characterized by X-ray Diffraction (Bruker AXS D8 DAVINCI) with Cu-Ka radiation (λ=1.5406 Å).
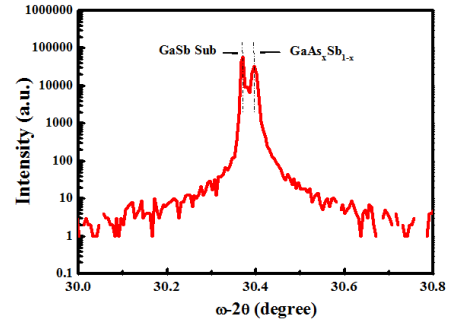
III. RESULTS AND DISCUSSION

Figure 1. HRXRD pattern of GaAs0.03Sb0.97 alloy sample..

Fig. 1 shows the high resolution X-ray diffraction (HRXRD) curve of the GaAsSb alloy samples. The diffraction peaks positioned at 30.371° and 30.396° is assigned to the GaSb substrate and $GaAs_xSb_{1-x}$ alloy layer, respectively. $GaAs_xSb_{1-x}$ alloy layer has narrower FWHM, it is indicated that the crystalline quality of the $GaAs_xSb_{1-x}$ layer is satisfactory. The component of the $GaAs_xSb_{1-x}$ alloy can be calculated by formula [16]:

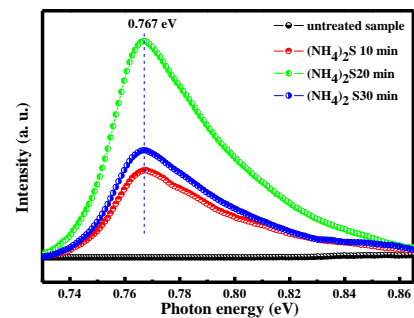$$\alpha_{alloy}=\alpha_{GaAs}\, x+\alpha_{GaSb}(1-x)$$

where α is lattice constant. The α_{alloy} can be calculated by Bragg's law:

$$2d\sin\theta = n\lambda$$

where n is a positive integer, λ is the wavelength of incident wave and d is the interplanar distance. Due to $GaAs_xSb_{1-x}$ alloy is cubic crystal system, the interplanar distance can be calculated by formula:
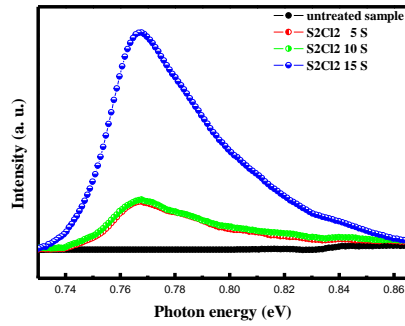
$$d=$$

Therefore, the x is equal to 0.03.

Figure 2. (a) The PL spectrum of GaAs0.03Sb0.97 passivated by (NH4)2S for 10, 20 and 30 min. (b) The PL spectrum of GaAs0.03Sb0.97 passivated by S2Cl2 for 5, 10 and 20s.

The energy gap of GaSb is 0.75eV. By adjusting the substrate component, the band gap of GaAsxSb1-x can controlled. The band gap of GaAsxSb1-x can be calculated by formula: $gGaAsxSb1-x=gGaSbx+gGaAs(1-x)$ where g is band gap. The calculating data indicate that, the band gap of GaAs0.03Sb0.97 is 0.767 eV. It can be observed that all PL peaks have the same position at 0.767 eV. The value of calculation is good to worth with actual measurement.

Fig. 2(a) shows the PL spectra of GaAs0.03Sb0.97 substrate and GaAs0.03Sb0.97 passivated by (NH4)2S for 10, 20 and 30 min. It can be seen that the PL intensity of the GaAs0.03Sb0.97 substrate is almost zero, and (NH4)2S-treated samples showed obvious emission peaks located at 0.767 eV. This phenomenon indicates the sulfur treatment is an effective passivation method for reducing surface states density of III-V compounds. Oxide layer is very easy to form on the surface under atmospheric conditions [17]. During sulfur treatment, the sulfur atoms are strongly chemisorbed and occupied the active surface sites because of its lower heat of formation. In fact, the O-bonds on the surface of the materials seem to be replaced, at least partly, by S-bonds after sulfur passivation [18].

The PL intensity is strongly dependent on (NH4)2S passivation time. Initially, the PL intensity increased with time increased. When passivation time is 20 min, GaAs0.03Sb0.97 sample had the strongest PL emission. Then, the PL intensity decreased with the passivation extending. It is due to forming a thick sulfur atomic layer to reduce the recombination centers of excitions [19, 20]. As shown in the Fig. 2(b), the passivation by S2Cl2 solution has the same effect. By S2Cl2 solution passivation, the PL intensity of the GaAs0.03Sb0.97 surface has been enhanced obviously. When passivation time is 10s, the PL intensity reaches a maximum and then the PL intensity dropped swiftly.
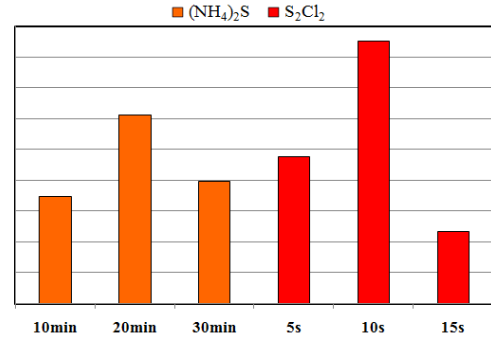

Figure 3. Relative PL peak intensity of the samples in different passivation conditions

Fig. 3, it can be seen that the PL intensity of the GaAs0.03Sb0.97 surface which are treated by (NH4)2S and S2Cl2 solution. The peak intensity of the 10s S2Cl2-treated sample is about 1.4 times larger than the 20 min (NH4)2S-treated sample. Compare with (NH4)2S treatments, S2Cl2 treatments have the higher PL intensity and shorter immerse time. And, S2Cl2 passivation solution don't need to heat. However, S2Cl2 treatments are more susceptible to the passivation time than (NH4)2S treatments. The time control of S2Cl2 passivation for samples needs exceedingly accurate.
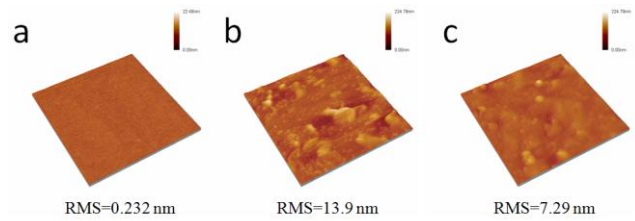

Figure 4. Measured by the AFM surface roughness of the sample icon.(a) untreated, (b)passivated by (NH4)2S for 20 min, (c)passivated by S2Cl2 for 10s..

Choose the samples with strongest PL intensity in two methods to be compared. Fig. 4 shows the AFM test results of GaAs0.03Sb0.97 substrate, (NH4)2S-treated and S2Cl2-treated samples. It is clearly that the surface of GaAs0.03Sb0.97 substrate is very smooth. The surface roughness of RMS (Root Mean Square) is 0.232nm. The surface morphologies of passivated GaAs0.03Sb0.97 sample became rougher. For the 20 min (NH4)2S-treated sample and the 10s S2Cl2-treated sample, the RMS are 7.29 nm and 13.9 nm, respectively. The reason of this phenomenon could be due to the etching reaction of the alkaline solution and the deposition of polycrystalline sulfur. It is clearly that the roughness of the S2Cl2 treated sample is smaller than the (NH4)2S treated.

IV. CONCLUSIONS

In order to study the properties of GaAsSb alloy by (NH4)2S and S2Cl2 treatment, grows GaAs0.03Sb0.97 by MBE, then (NH4)2S and S2Cl2 solution is used to passivate the surfaces of GaAsSb alloy. XRD spectrum indicated that the crystalline quality of GaAs0.03Sb0.97 substrate is satisfactory. Compared with the pristine sample, the PL intensity of GaAs0.03Sb0.97 by two

passivating agents has increased significantly. The PL intensity is strongly dependent on passivation time. For the (NH4)2S and S2Cl2 treatments, the optimum passivation time is around 20 min and 10s, respectively. The PL intensity of the 10s S2Cl2-treated sample is about 1.4 times larger than the 20 min (NH4)2S-treated sample. Meanwhile, AFM images indicated that the roughness of the S2Cl2-treated sample is smoother than the (NH4)2S-treated sample. Comparing to PL intensity and surface roughness, S2Cl2 treatments have a greater efficiency. However, due to more susceptible to the passivation time, S2Cl2 treatment needs to be extra accurate. In conclusion, S2Cl2 passivation is a more effective method in improving the optical properties of GaAs0.03Sb0.97 material, which is then conducive to the development of GaAsSb-based optoelectronic devices.

REFERENCES

[1] Lebedev, M. V., Kunitsyna, E. V., Calvet, W., Mayer, T., & Jaegermann, W, "Sulfur passivation of GaSb (100) surfaces: comparison of aqueous and alcoholic sulfide solutions using synchrotron radiation photoemission spectroscopy," The Journal of Physical Chemistry C, 117(31), July 2013, pp. 15996–16004. doi: 10.1021/jp401942p.

[2] Canedy, C., Boishin, G., Bewley, W., Kim, C., Vurgaftman, I., Kim, M., Whitman, L. "Correlating growth conditions with photoluminescence and lasing properties of mid-IR antimonide type II "W" structures," Journal of Vacuum Science & Technology B, 22(3), June 2004, pp. 1575-1579, doi: 10.1116/1.1688805.

[3] Steinle, G., Riechert, H., & Egorov, A. Y., "Monolithic VCSEL with InGaAsN active region emitting at 1.28 μm and CW output power exceeding 500 μW at room temperature," Electronics Letters, 37(2), January 2001, pp. 93-95, doi: 10.1049/el:20010098.

[4] Yamada, M., Anan, T., Kurihara, K., Nishi, K., Tokutome, K., Kamei, A., & Sugou, S., "Room temperature low-threshold CW operation of 1.23 μm GaAsSb VCSELs on GaAs substrates," Electronics Letters, 36(7), March 2000, pp. 637-638, doi: 10.1049/el:20000483.

[5] Liu, Z., Hawkins, B., & Kuech, T, Chemical and structural characterization of GaSb (100) surfaces treated by HCl-based solutions and annealed in vacuum. Journal of Vacuum Science & Technology B, 21(1), December 2003, pp. 71-77, doi: 10.1116/1.1532023.

[6] Lin, C. L., Su, Y. K., Se, T. S., & Li, W. L, "Variety transformation of compound at GaSb surface under sulfur passivation," Japanese Journal of Applied Physics, 37(12B), December 1998, pp. L1543-L1545, doi: 10.1143/JJAP.37.L1543

[7] Tajik, N., Haapamaki, C., & LaPierre, R., "Photoluminescence model of sulfur passivated p-InP nanowires," Nanotechnology, 23(31), August 2012, pp. 315703-315708, doi:10.1088/0957-4484/23/31/315703

[8] Gin, A., Wei, Y., Bae, J., Hood, A., Nah, J., & Razeghi, M. , "Passivation of type II InAs/GaSb superlattice photodiodes," Thin Solid Films, Volumes 447–448, January 2004, pp. 489-492, doi:10.1016/j.tsf.2003.09.00

[9] Plis, E., Rodriguez, J.-B., Lee, S., & Krishna, S. (2006). Electrochemical sulphur passivation of InAs/GaSb strain layer superlattice detectors. Electronics Letters, 42(21), October 2006, pp. 1248-1249, doi: 10.1049/el:20062495.

[10] Rehm, R., Walther, M., Fuchs, F., Schmitz, J., & Fleissner, J. (2005). Passivation of InAs/(GaIn) Sb short-period superlattice photodiodes with 10 μm cutoff wavelength by epitaxial overgrowth with AlxGa1-xAsySb1-y. Applied Physics Letters, 86(17), April 2005, pp. 173501-173503, doi: 10.1063/1.1906326.

[11] Hood, A., Delaunay, P.-Y., Hoffman, D., Nguyen, B.-M., Wei, Y., Razeghi, M., & Nathan, V., "Near bulk-limited R0A of long-wavelength infrared type-II InAs/GaSb superlattice photodiodes with polyimide surface passivation," Applied Physics Letters, 90(23),June 2007, pp. 233513.1-233513.3, doi: 10.1063/1.2747172.

[12] Martens, K., Wang, W., De Keersmaecker, K., Borghs, G., Groeseneken, G., & Maes, H., "Impact of weak Fermi-level pinning on the correct interpretation of III-V MOS CV and GV characteristics," Microelectronic engineering, 84(9), October 2007, pp. 2146-2149, doi:10.1016/j.mee.2007.04.039

[13] Zhao, H., Shahrjerdi, D., Zhu, F., Kim, H.-S., Injo, O., Zhang, M., Lee, J. C., "Inversion-type InP MOSFETs with EOT of 21 Å using atomic layer deposited Al2O3 gate dielectric," Electrochemical and solid-state letters, 11(8), June 2008, H233-H235, doi:10.1149/1.2938728.

[14] Yablonovitch, E., Sandroff, C., Bhat, R., & Gmitter, T., "Nearly ideal electronic properties of sulfide coated GaAs surfaces," Applied Physics Letters, 51(6), June 1987, pp. 439-441, doi: 10.1063/1.98415.

[15] Buehlmann, P., Bailat, J., Dominé, D., Billet, A., Meillaud, F., Feltrin, A., & Ballif, C, "In situ silicon oxide based intermediate reflector for thin-film silicon micromorph solar cells," Applied Physics Letters, 91(14), October 2007, pp. 143505.1-143505.3, doi: 10.1063/1.2794423.

[16] Villaggi, E., Bocchi, C., Armani, N., Carta, G., Rossetto, G., & Ferrari, C, "Deviation from vegard law in lattice-matched InGaAs/InP epitaxial structures," Japanese Journal of Applied Physics, 41(2S), February 2002, pp. 1000-1003, doi:10.1143/JJAP.41.1000.

[17] Salesse, A., Alabedra, R., Chen, Y., Lakrimi, M., Nicholas, R., Mason, N., & Walker, P., "Improved photoluminescence from electrochemically passivated GaSb," Semiconductor science and technology, 12(4), April 1997, pp. 413-418, doi:10.1088/0268-1242/12/4/013.

[18] Dutta, P., Sangunni, K., Bhat, H., & Kumar, V., "Sulphur passivation of gallium antimonide surfaces," Applied Physics Letters, 65(13), July 1994, pp. 1695-1697, doi: 10.1063/1.112889.

[19] Eftekhari, G., "Electrical properties of sulfur-passivated III–V compound devices," Vacuum, 67(1), September 2002, pp. 81-90, doi:10.1016/S0042-207X(02)00195-1.

[20] Chioncel, M., Díaz-Guerra, C., & Piqueras, J., "Luminescence from indented Te-doped GaSb crystals," Semiconductor science and technology, 19(3), March 2004 , pp. 490-493, doi:10.1088/0268-1242/19/3/036.