Passivation of GaAs surface by sulfur glow discharge

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(Received 29 April 1996; accepted for publication 21 June 1996)

A new sulfur passivation technique, the sulfur vapor glow discharge, has been developed to form a thick sulfide layer on GaAs surface. By using Auger electron spectroscopy and x-ray photoelectron spectroscopy measurements, the main composition of the passivation layer is found to be gallium sulfide without the existence of unstable As–S bonds. The stability of the passivation effect is demonstrated by the nondecaying behavior of the photoluminescence intensity of the GaAs passivation surface under the illumination of the laser beam with very high intensity. © *1996 American Institute of Physics.* [S0003-6951(96)00936-9]

Sulfur treatment of GaAs surface developed by Sandroff *et al.*[1] seems to be the most promising technique in solving the problem of surface passivation of GaAs materials and devices.[2–6] The ordinary method by dipping GaAs in Na_2S or $(NH_4)_2S$ aqueous solution was proved to be unstable. Its passivation effect was lost after the sample was exposed in air for a period of time especially under the illumination of light beam.[7] The main factor which causes the failure of passivation is the replacement of Ga–S bonds by As–O and Ga–O bonds on the surface. Na_2S or $(NH_4)_2S$ dipping could only form one monolayer of sulfur atoms bonded to surface Ga and As atoms, which are easily reoxidized in air. To solve the problem of unstability, several approaches have been proposed. The key point is to form a thick robust sulfide layer on the GaAs surface, which can prohibit the reoxidation of Ga–S bonds. The electrochemical sulfur passivation developed by Hou *et al.* has been illustrated to be a very stable and long lived passivation technique.[8,9] MacInnes *et al.*[10] employed the metalorganic chemical vapor deposition (MOCVD) of $[C(CH_3)_3GaS]_4$ on GaAs to form a very stable GaS passivating thin film. In this work, we develop a new passivation method, the sulfur vapor glow discharge (SGD) technique, which could use a relatively simple facility to sulfurize the GaAs surface by forming a stable passivation layer. The composition and the passivation effect of the sulfide layer formed on the GaAs surface were investigated by using Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), and photoluminescence (PL) measurements.

The samples used were semi-insulating GaAs(100) single-crystal wafers. The surface cleaning was performed by ultrasonically washing in acetone, ethanol, and deionized water in sequence for 5 min each and drying by spinning. The experimental setup for SGD is shown in Fig. 1. The sample was put on the top (open end) of a double wall glass tube with the inner length of 150 mm and the inner diameter of 14 mm. The spectroscopically pure sulfur powder filled the bottom part of the inner glass tube. A thin metal rod fixed on the sidewall of the tube was used as the anode for discharging, while the sample was used as the cathode. The whole tube was installed inside a vacuum chamber which was pumped down to the pressure of 10^{-2} Pa before discharging. The sample was heated to 400 °C by resistance heating of a tungsten coil at its back side. The temperature was measured by a thermocouple placed at the backside of the GaAs wafer. The sulfur vapor was produced by heating the glass tube with a tungsten coil wound outside it. The vapor pressure of sulfur inside the tube was maintained at about 10 Pa. A high voltage was then applied between the anode and the cathode. The glow discharge was initiated at the voltage of 2 kV first and then preserved at 800 V. A blue color fluorescence was observed during the glow discharge. The discharging process was undergone for about 30 min.

The purpose of using SGD is to form a gallium sulfide layer on the GaAs surface by the chemical reaction between activated sulfur and the surface Ga atoms. Sulfur has high vapor pressure, which could reach 10 Pa at the temperature of 100 °C. However, elemental sulfur exists in the form of S_8 rings,[11] which hardly react with other elements to form sulfides below the temperature of 600 °C. Ashby *et al.*[12] reported a photosulfidation technique for GaAs, in which the

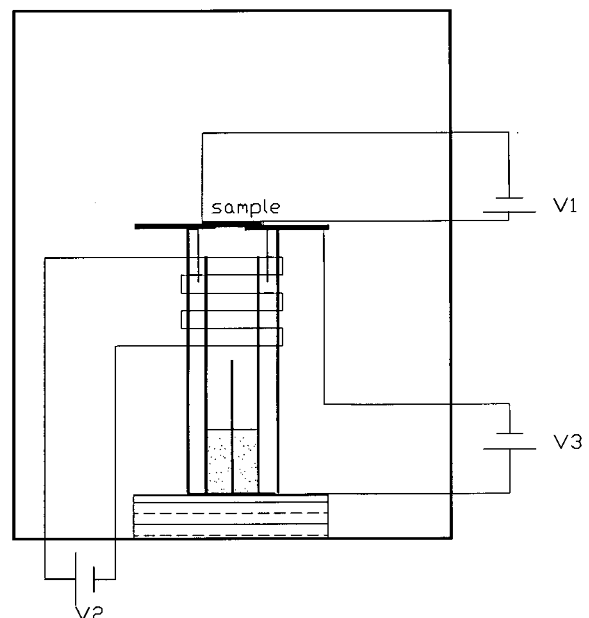

FIG. 1. Schematic diagram of the sulfur glow discharge setup.

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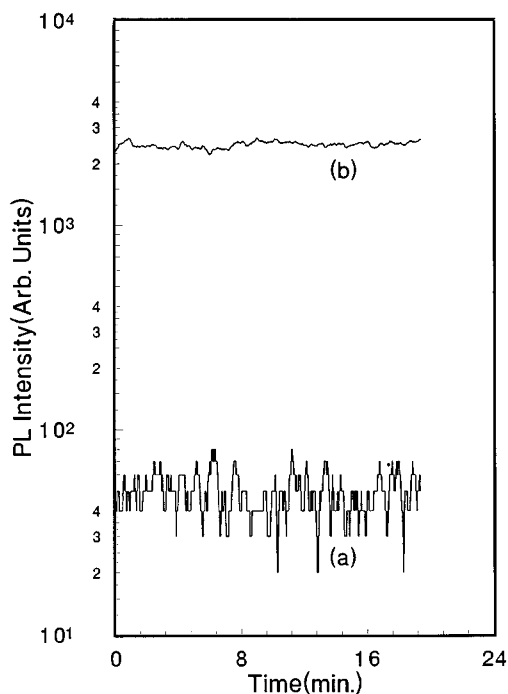

FIG. 2. PL intensity vs the laser illumination time of GaAs(100), (a) treated by $5H_2SO_4:1H_2O_2:1H_2O$, (b) passivated by sulfur glow discharge.

ultraviolet radiation was used to break the S_8 rings of elemental sulfur vapor and a thin sulfide layer with the thickness of about 0.8 nm containing arsenic sulfide was formed. In this work, the sulfur plasma created by glow discharge is chemically reactive enough to combine with the surface atoms on GaAs at relatively low temperatures. Previous studies have shown that the S passivation is benefited by the formation of Ga–S bonds, while the As–S bond is unstable.[13,14] By thermally annealing the S treated GaAs in vacuum at temperatures above 360 °C, the As–S bonds on the surface are fully dissociated, while the Ga–S bonds are stable even at the temperature of 500 °C or higher.[13,14] To avoid the formation of As–S bonds during the glow discharge, it is thus suitable to keep the GaAs wafer at the temperature of 400 °C. After passivation by glow discharge, the sample surface shows a blue interference color. Under proper discharge condition, the surface could remain flat and mirrorlike.

The passivation effect was checked by PL measurements, which were performed at room temperature by using a Jobin Yvon Spectrometer with the 514 nm line of an Ar^+ laser as the light source. The power density on the sample surface was about 1.6 kW/cm^2, i.e., 100 mW in a spot size of 90 μm diameter. For comparison, a GaAs sample treated by ordinary cleaning method ($5H_2SO_4:1H_2O_2:1H_2O$) was taken as the reference. The PL intensity at the wavelength of 870 nm, i.e., the wavelength of the GaAs luminescence peak, was measured as a function of laser illumination time. The results are shown in Fig. 2. Both the enhancement and the stability of the PL intensity from the S passivated GaAs are illustrated. It could be noted that the power density used in this work is about three orders of magnitude larger than that used by MacInnes *et al.*[10] The longevity of the passivation

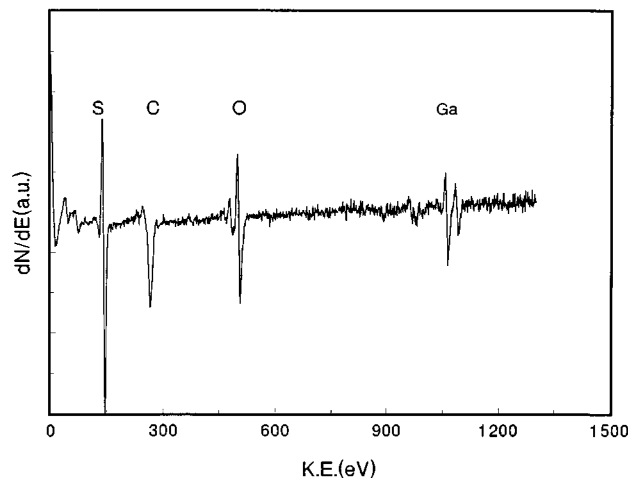

FIG. 3. AES spectra of the sample treated by sulfur glow discharge.

was also illustrated by measuring the PL intensities of the samples after being stored in atmospheric ambient for 3 months. The PL intensity of the S-passivated sample is stronger by 50–70 times than that of the reference sample.

AES spectrum and its depth profile of the sample are shown in Figs. 3 and 4. It can be seen that the passivating film contains basically S and Ga. The C and O signals come from the contamination and native oxide on the surface formed by exposure in air and could be removed after ion sputtering for 3 min. The As content in the passivating layer is less than 10%. According to the sputtering rate, the thickness of the passivating layer is about 100 nm.

To identify the chemical states of S in the passivating layer, the Ga $2p_{3/2}$ core level XPS peaks were measured under the excitation of an Al K_α x-ray source with the photon energy of 1486.6 eV. The As $2p_{3/2}$ XPS signal is not detectable in the film, while the S $2p$ signal is overlapped with the Ga $3s$ peak and thus could not be discriminated. Figure 5 shows the experimental spectra of Ga $2p$, where curve (a) was taken after the surface was sputtered by Ar^+ ions to remove the native oxide and the contamination, curve (b) was taken near the interface between the passivation layer and the GaAs substrate. By using curve fitting, the

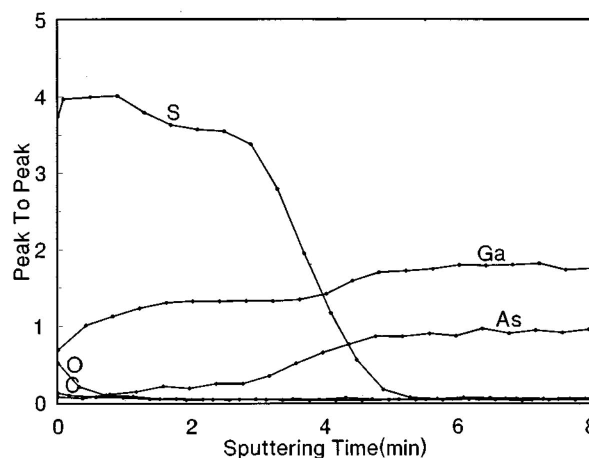

FIG. 4. AES depth profile of the sample treated by sulfur glow discharge.

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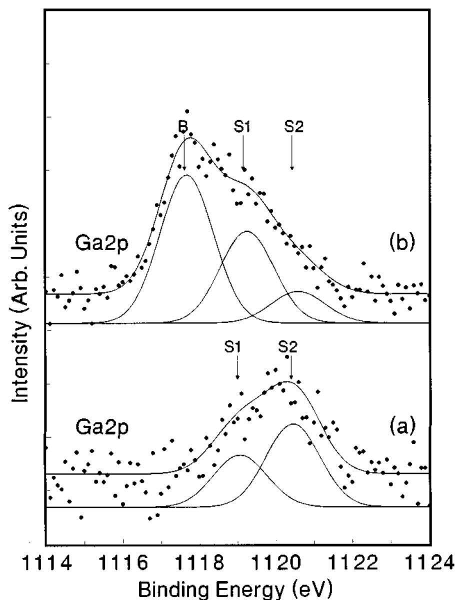

FIG. 5. Ga2*p* XPS core level spectra of the sample treated by glow discharge, (a) taken at the surface of the sample after ion sputtering to remove the native oxide and contamination, and (b) taken at the interface between the passivation layer and the GaS substrate.

experimental data (circles) can be separated into several peaks with different binding energies [lower curves in (a) and (b)]. The peak B at the lowest binding energy of 1117.7 eV is originated from the Ga atoms bonded with As in the GaAs substrate. Other two peaks S_1 and S_2 are believed to be related with the Ga atoms in different sulfurized states. Peak S_2 has a chemical shift of 2.91 eV with respect to the bulk peak B. It agrees with the sulfurized Ga peak found in the electrochemically passivated GaAs surface. The chemical shift of peak S_1 is 1.57 eV, which is a little larger than 1.3 eV of the peak observed in electrochemically passivated sample. The peak S_1 has also been found in our previous XPS measurements of S_2Cl_2 treated GaAs surface.[15] MacInnes *et al.* measured the Ga $3p_{3/2}$ XPS peaks of the CVD GaS films. The experimental binding energy of 106.8 eV they observed was explained to correspond to the Ga $3p_{3/2}$ of Ga_2S_3 compound. This value is about 1.6 eV higher than the binding energy of Ga $3p_{3/2}$ in GaAs.[16] Thus we believe that the peak with chemical shift of 1.57 eV in our sample comes from Ga_2S_3, while the peak with the highest chemical shift of 2.9 eV corresponds to another sulfurized Ga state with more charge transfer from Ga to S, most probably Ga_2S_5. From curves (a) in Fig. 5, it could be seen that the latter compound dominates in the outer part of the passivation film and may play the major role in regard to the longevity of the passivation.

By being compared with the MOCVD method of Mac Innes *et al.*, SGD is a sulfurization process by pure S on the GaAs surface. Whereas in MOCVD, the sulfide overlayer is deposited by the decomposition of some chemical species on the top of the GaAs substrate. The interfacial properties such as the chemical bonds, interfacial defects, and electronic states might be different between these two cases. It is well known that for the passivating Si surface, the formation of silicon dioxide (native oxide) by thermal oxidation is a better choice than the deposition of SiO_2 (oxide overlayer) by CVD. Similar to the thermal oxidation of Si, the thermal sulfurization method SGD might be a promising technique to passivate the GaAs surface in the process of the device fabrication.

In conclusion, by using sulfur vapor glow discharge, a stable GaS passivation layer can be formed on GaAs(100). The formation of unstable S–As bonds at the passivation layer/GaAs interface could be avoided by suitably choosing the substrate temperature during the glow discharge process. The thick and robust passivation layer could prevent the GaAs surface from being oxidized in air. The durability of the passivation effect is illustrated. It might be an interesting topic for further investigations that whether the method of creating ''native'' sulfide or those to deposit sulfide overlayer are in favor of the S-passivation of GaAs.

We wish to thank Professor J. T. Wang and Dr. J. Wang for fruitful discussions. This work was partially supported by the National Natural Science Foundation and the State Education Commission of China.

[1] C. J. Sandroff, R. N. Nottenberg, J. C. Bischoff, and R. Bhat, Appl. Phys. Lett. **51**, 33 (1987).
[2] M. R. Carpenter, M. R. Melloch, and T. E. Dungan, Appl. Phys. Lett. **53**, 66 (1988).
[3] J.-F. Fan, H. Oigawa, and Y. Nannichi, Jpn. J. Appl. Phys. **27**, L2125 (1988).
[4] M. S. Carpenter, M. R. Melloch, B. A. Cownas, Z. Dardas, and W. N. Delgass, J. Vac. Sci. Technol. B **7**, 845 (1989).
[5] M. S. Carpenter, M. R. Melloch, and M. S. Lundstrom, Appl. Phys. Lett. **52**, 2157 (1988).
[6] B. J. Skromme, C. J. Sandroff, E. Yablonovitch, and T. Gmitter, Appl. Phys. Lett. **51**, 2022 (1987).
[7] M. Oshima, T. Scimeca, Y. Watanabe, H. Oigawa, and Y. Nannichi, Extended Abstracts of 22nd International Conference on Solid State Devices and Materials, 1992, p. 545.
[8] X. Y. Hou, W. Z. Cai, Z. Q. He, P. H. Hao, Z. S. Li, X. M. Ding, and X. Wang, Appl. Phys. Lett. **60**, 2252 (1992).
[9] Z. S. Li, X. Y. Hou, W. Z. Cai, W. Wang, X. M. Ding, and X. Wang, J. Appl. Phys. **78**, 2764 (1995).
[10] A. N. MacInnes, M. B. Power, and A. R. Barron, Appl. Phys. Lett. **62**, 713 (1993).
[11] J. E. Bear and M. Carmack, J. Am. Chem. Soc. **71**, 1215 (1945).
[12] C. l. H. Ashby, K. R. Zavadil, A. J. Howard, and B. E. Hammons, Appl. Phys. Lett. **64**, 2388 (1994).
[13] H. Hirayama and Y. Matsumoto, Appl. Phys. Lett. **54**, 2565 (1989).
[14] H. Sugahara, M. Oshima, and R. Klauser, Surf. Sci. **242**, 335 (1991).
[15] Z. S. Li, W. Z. Cai, R. Z. Su, G. S. Dong, D. M. Huang, X. M. Ding, X. Y. Hou, and X. Wang, Appl. Phys. Lett. **64**, 3425 (1994)
[16] *Handbook of X-ray Photoelectron Spectroscopy*, edited by C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder, and G. E. Muilenberg (Perkin-Elmer Physical Electronics Division, 1978).

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