S₂Cl₂ treatment: A new sulfur passivation method of GaAs surface

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We have developed a new sulfur passivation method—S_2Cl_2 treatment, which is quite effective for removing the surface oxide layer of GaAs and passivating the surface with monolayer thick sulfides. Photoluminescence (PL) spectroscopy, Auger electron spectroscopy (AES), and x-ray photoelectron spectroscopy (XPS) are used to study the passivated GaAs (100) surfaces. The results of PL reveal that the PL intensity increases by two orders of magnitude, which is indicative of the reduction of surface recombination velocity of GaAs by this treatment. AES data prove that the sulfurized surface contains S, Ga, As, C, and small amount of Cl atoms but no oxygen signal at all. XPS study shows that sulfur atoms bond to both Ga and As atoms more effectively on S_2Cl_2 treated surfaces than those passivated by $(NH_4)_2S_x$.

The passivation of GaAs surfaces is one of the key problems in III-V semiconductor device technology. The basic purpose is to replace the GaAs native oxide on the surface with some kind of passivation layer which can significantly reduce the density of surface states and thus remove the Fermi level pinning, resulting in the reduction of surface recombination velocity and improvement of device performance. Nowadays, the most popular method developed for passivating GaAs is the $(NH_4)_2S_x$ dipping treatment, which can form a sulfur-passivated GaAs surface with about one monolayer (ML) of S atoms bonded to surface Ga atoms.[1–6] However, the $(NH_4)_2S_x$ treatment requires a relatively long time, i.e., several tens of hours at room temperature or 30–60 min at elevated temperature of 60 °C. During that period, the oxygen species contained in the $(NH_4)_2S_x$ aqueous solution would inevitably react with the GaAs surface, resulting in the replacement of Ga—S bonds and thus causing the partial failure of S passivation. In this work, we develop a new S-passivation technique by using an oxygen-free solution S_2Cl_2 instead of $(NH_4)_2S_x$ aqueous solution. The results show that the S_2Cl_2 is very effective in removing the native oxide of GaAs and passivates the surface with fast and controllable rate. It could be used as an alternative to $(NH_4)_2S_x$ or Na_2S $9H_2O$ for a routine S-passivation process.

n-type Te-doped GaAs (100) single crystal wafers with a doping concentration of $1×10^{16}$ cm^{-3} were chemically cleaned ultrasonically by acetone, ethanol, and de-ionized water for 5 min each and dried by flow nitrogen. The S passivation was carried out by dipping the wafer in S_2Cl_2 for 5 s or the diluted $S_2Cl_2+CCl_4$ solution for a longer time. Both treatments gave rise to the same results. The effect is found to remove the native oxide and form a S-passivation layer. To remove the residual S_2Cl_2 on the surface, the wafer was rinsed by CCl_4 first and then by acetone, ethanol, and de-ionized water sequentially. The CCl_4 rinse plays a very important role, i.e., to avoid the quick reaction of S_2Cl_2 with water molecules which will result in the failure of passivation. The residual CCl_4 is quite inert and soluble in acetone.

It will not cause additional contamination if the above process is carefully handled. The sample was then loaded into the ultrahigh vacuum (UHV) chamber of an electron spectrometer to do the characterization. In addition, the surfaces of three GaAs wafers, without chemical treatment, treated by $H_2SO_4:H_2O_2:H_2O=5:1:1$ at 60 °C for 10 s, and treated by $(NH_4)_2S_x$ solution dipping at room temperature for 15 h, were also measured for comparison.

The surface compositions of treated and untreated samples were measured by x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). The light source of XPS was the Al $k\alpha$ line with a photon energy of 1486.6 eV. The primary electron energy of AES was 3 keV. The base pressure of the UHV chamber was $3×10^{-10}$ mbar. The photoluminescence (PL) intensity of a GaAs wafer is indicative of the surface recombination velocity. The PL measurements were carried out by a Jobin–Yvon U-1000 Raman spectrometer with the 514 nm line of an Ar$^+$ laser as the excitation source. The laser power density on the sample surface was 1.5 kW/cm^2.

Figure 1 shows the AES of three samples. Comparing the spectra (a), (b), and (c), the relative peak-to-peak inten-
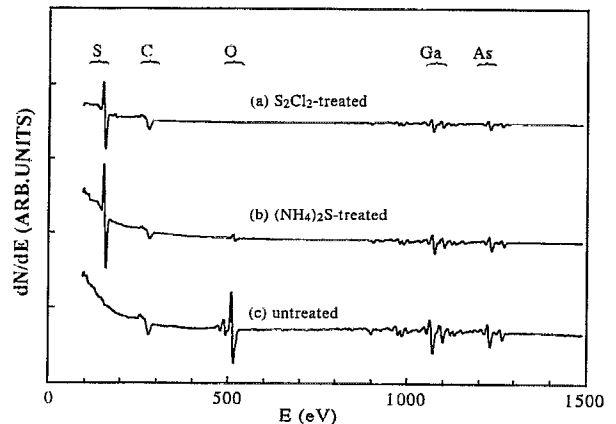

FIG. 1. AES spectra for (a) Si_2Cl_2-treated, (b) $(NH_4)_2S_x$-treated, and (c) untreated GaAs(100) surfaces.

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TABLE I. Relative peak-to-peak intensities of components in AES spectra.

| Passivation method	AES peak-to-peak height					
	S	Cl	C	O	Ga	As
S_2Cl_2	5.52	0.28	1.19	0	1	0.68
$(NH_4)_2S_x$	5.56	0	0.61	0.34	1	0.75
untreated	0	0	0.59	2.09	1	0.69

FIG. 2. Effect of thermal annealing on the C desorption of S_2Cl_2-passivated GaAs surface. (a) Room temperature, (b) 300 °C, (c) 500 °C, and (d) 600 °C.

sities of components with respect to that of Ga are listed in Table I. The peak ratios of As to Ga are about the same for these three samples. The peak ratios of S to Ga are quite close for the two S-passivated samples, which implies that the thickness of S-containing layers for a S_2Cl_2 treated sample is about the same of that for the $(NH_4)_2S_x$ treated surface. A small amount of Cl remains on the surface of the S_2Cl_2 treated sample. The Cl atoms are believed to be weakly bonded to the surface atoms and could be desorbed quickly under the irradiation of an electron beam during the AES measurements. The most significant effect of S_2Cl_2 treatment is the lack of O KLL signal, as seen from curve (a). It has been found that even the S_2Cl_2 treated sample was exposed in atmosphere for tens of minutes or immersed in de-ionized water for 40 h, the O KLL signal was still below the detection limit of AES. In general, if a sample surface was transferred from air into the UHV chamber, a very thin native oxide film and surface oxygen contaminations are inevitably formed. We suggest the explanation of the lack of oxygen uptake as follows. First, the S_2Cl_2 solution is a very strong etchant of the GaAs native oxides. The etching rate of oxides by S_2Cl_2 is measured to be 18 nm/s, which is about four times larger than that of GaAs. Thus, the native oxides of GaAs substrate are rapidly removed. Second, the passivation process is completed within a very short time interval, so the foreign atom contamination is not significant during such a short time period. Note that the purity of the S_2Cl_2 solution we used was only chemically pure. Third, the small amount of remaining Cl on the surface, which comes from the chloride itself, may play the role of protecting the uptake of oxygen. The C signal on the S_2Cl_2 treated sample is relatively large, which is believed due to the impurity of the S_2Cl_2 solution. From our XPS measurements (not shown here), the peak position and line shape of $C1s$ are the same as that of $C1s$ from a naturally contaminated surface. Also, the relative intensity of $C1s$ was enhanced as the ejection angle of photoelectrons increased. All the facts implied that the carbon is chemically adsorbed on the top of the passivated surface. By heating the sample above 500 °C, the C signal disappears, as shown in Fig. 2.

XPS measurements show the chemical states of S atoms. Since the $S2p$ core level peak overlaps with the $Ga3s$ and is not able to be identified, we take the line shapes of $Ga2p$ and $As2p$ as the fingerprints of their sulfurized states. The electron escape depths of $Ga2p$ and $As2p$ photoelectrons are about 0.8 nm, so the information obtained is surface sensitive. The results are shown in Figs. 3(a) and 3(b) for the two S-passivated samples. By curve fitting, the S_2Cl_2 treated sample (a) shows the two peak structures in both $Ga2p$ and $As2p$ core level spectra. The chemically shifted peaks are
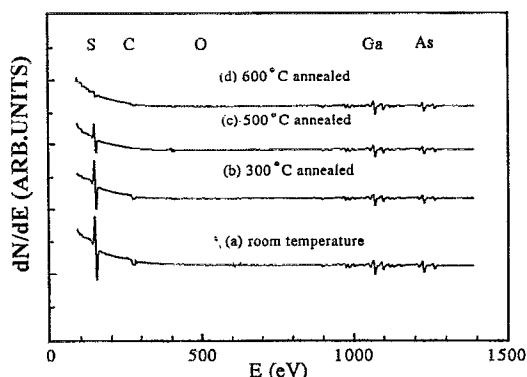
contributed by the Ga—S and As—S bonds, with the peak shifts of 1.3 and 1.54 eV towards higher binding energies with respect to that of $Ga2p$ and $As2p$ in GaAs. For the $(NH_4)_2S_x$ treated sample, the Ga—S bonds are relatively weak with a chemical shift of only 0.55 eV[7] and thus could not be identified in Fig. 3. The ratios of intensities (peak areas) of As—S bond to As—Ga bond for these two S-passivated samples are 0.60 and 0.26, respectively. Thus, we conclude that the S atoms bond to surface Ga and As atoms more completely for S_2Cl_2 treated samples than for the $(NH_4)_2S_x$ treatment. However, it has been verified that the surface passivation effect of S treatment is mainly attributed to the formation of Ga—S bonds. For our S_2Cl_2 treated sample, the intensity of the Ga-S peak is 17% of that of Ga—As bonds. Comparing with the anodic sulfurized GaAs surface,[8] which is a very stable passivated surface, the ratio of Ga-S peak to Ga-As peak in our present case is rather small. Moreover, the chemical shift of $Ga2p$ for the anodic sulfurized sample could reach the values of 1.3, 2.8, and 4.4 eV. The latter two strongly bonded Ga-S states are not observed here.

The passivation effect of S treatments is measured by the photoluminescence. The PL intensities versus Ar^+ laser irra-
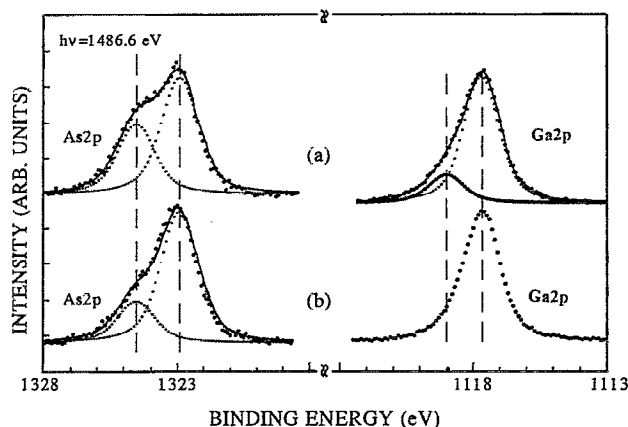

FIG. 3. $As2p$ and $Ga2p$ XPS core level spectra of (a) S_2Cl_2-passivated and (b) $(NH_4)_2S_x$-passivated GaAs(100) surfaces. Open circles—experimental data, dotted curves—separated components by curve fitting.
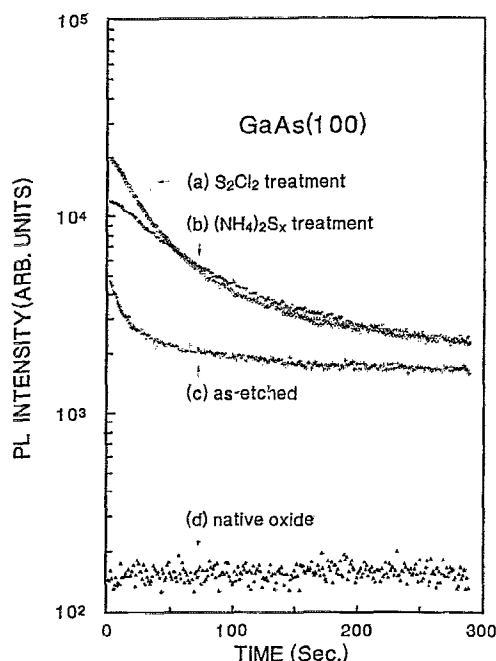
FIG. 4. The PL spectra of GaAs(100). (a) S_2Cl_2-treated, (b) $(NH_4)_2S_x$-treated, (c) as-etched, and (d) untreated.

diation time for four different samples are shown in Fig. 4. The initial PL intensities of S_2Cl_2 treated and $(NH_4)_2S_x$ treated samples are enhanced by two orders of magnitude as compared with the GaAs surface covered with native oxide. The S_2Cl_2 treated sample seems to possess the lowest surface recombination velocity. However, under the irradiation of a laser beam at the power density of 1.5 kV/cm^2 for 5 min, the PL intensity drops down to about one tenth of its initial value. The degradation of S_2Cl_2 passivation originates from the reoxidation of the GaAs surface speeded by the laser

irradiation. The same situation occurs for $(NH_4)_2S_x$ treated GaAs surface.[9] This problem may be solved by depositing a robust GaS overlayer on the S passivated surface.[10] Therefore, the S_2Cl_2 passivation method might be of practical use in GaAs device technology.

In summary, we developed a new sulfur passivation method by using an oxygen-free solution $S_2Cl_2+CCl_4$. The advantages of S_2Cl_2 treatment over the ordinary $(NH_4)_2S_x$ treatment are the freedom from oxygen uptake, more effective removal of the native oxide, formation of stronger Ga—S bonds, very short reaction time, and the adjustable etching rate of the GaAs surface by changing the concentration ratio of S_2Cl_2 to CCl_4.

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