Property Improvement of GaAs Surface by 1-Octadecanethiol Passivation

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Abstract: In this study the effects of 1-Octadecanethiol (ODT, 1-CH$_3$ [CH$_2$]$_{17}$SH) passivation on GaAs (100) surface and GaAs/Al$_2$O$_3$ MOS capacitors are investigated. The results measured by X-ray photoelectric spectroscopy (XPS), Raman spectroscopy and scan electron microscopy (SEM) show that the ODT passivation can obviously suppress the formation of As-O bonds and Ga-O bonds on the GaAs surface and produce good surface morphology at the same time, and especially provide better protection against environmental degradation for at least 24 h. The passivation time is optimized by photoluminescence (PL), and the maximum enhancement of PL intensity was 116%. Finally, electrical property of a lower leakage current was measured using the metal-oxide-semiconductor capacitor (MOSCAP) method. The results confirm the effectiveness of ODT passivation on GaAs (100) surface.

Keywords: GaAs; passivation; XPS; RAMAN; PL

1. Introduction

Controlling the chemical and electronic properties of the III-V semiconductor surface/interface by a passivation method is a theme that has been studied extensively in the fields of semiconductor lasers [1,2], metal-oxide-semiconductor field effect transistors [3,4], and solar batteries [5] for several decades. Among various methods, sulfur passivation, e.g., using CH$_3$CSNH$_2$, (NH$_4$)$_2$S·9H$_2$O, S$_2$Cl and Na$_2$S [6–8] aqueous or organic solutions, have been reported widely due to their simplicity and effectiveness. They can reduce the GaAs surface state density by removing Ga-O/As-O bonds and then saturate the dangling bonds with S-. But this sulfur passivation has the prominent drawbacks of poor environmental stability, metal contamination, and H$_2$S volatilization, which are averse to further applications.

In contrast, the passivation by long-chain thiols (C$_n$H$_{2n+1}$-SH, n ≥ 16) self-assembled monolayers (SAMs) [9] promises better stability in air exposure due to the thicker and denser sulfur-layer. H. A. Budz et al. reported that SAMs of octadecanethiol deposited on GaAs from liquid and vapor phases can inhibit the oxidation of the surface for an extended period of time [10,11]. In addition, H. A. Budz [11] and Shen Ye et al. [12] reported that SAMs of alkanethiol constructed on GaAs had a hydrophobic property. Pablo Mancheno-Posso et al. [13] reported the GaAs surface passivated by 1-eicosanethiol (ET-20 C, n = 20) without any reoxidation for 30 min air exposure. Daniel Cuypers [14] reported the GaAs surface passivated by sacrificial SAMs without Fermi level pinning in the center of the forbidden band.

In this work, we systematically investigate the impact of 1-Octadecanethiol (ODT-18 C, n = 20) passivation on the GaAs (100) surface through a combined of X-ray photoelectric spectroscopy (XPS, Escalab 250Xi, Thermo Fisher Scientific, Waltham, MA, USA), PL-Raman (LabRAM HR Evolution, Horiba Scientific, Paris, France) and scanning electron microscope (SEM, JSM-7610F, Japan

Electron Optics Laboratory, Tokyo, Japan) study. Finally, the leakage current was tested using a GaAs-MOSCAP structure.

2. Experiment

All substrates used in this study were Si-doped n-type (2.4×10^{18} cm^{-3}) GaAs (100) wafers. Prior to ODT (98%, Aladdin, Shanghai, China) passivation, samples were cleaned by sonication in acetone and ethanol for at least 5 min each, followed by a deionized water rinse and N$_2$ dry, then immersed in 5% hydrofluoric acid (HF, 40%, Aladdin, Shanghai, China) for 1 min to decrease the native oxides. To minimize air exposure after HF etching, the wafers were promptly transferred without drying to a 5 mL solution of the ODT in ethanol at room temperature for 24 h.

Next, XPS, Photoluminescence (PL), Raman and SEM measurements were used to investigate the impact of 1-Octadecanethiol passivation on the GaAs (100) surface. XPS was used to examine the bonding chemistry of the GaAs surface. XPS shown in this work was taken with monochromatic Al Kα radiation (1486.6 eV) with the anode operating at a power of 150 W, and the binding energy was corrected by the C 1s peak at 284.8 eV. PL-Raman spectra were recorded at room temperature using 532 nm laser excitation, and the acquisition time was set at 2 s. In order to establish reproducibility between measurements, a uniform untreated GaAs sample was used as a reference. We made sure that the deviation of the reference PL intensity in all measurements was kept within 10%. The electrical properties were evaluated by fabricating metal-oxide-semiconductor-capacitor (MOSCAP) with an Al (50 nm) electrode and Al$_2$O$_3$ (10 nm) insulator. All the parameters of the MOSCAP were identical except for the passivation. Here, the Al$_2$O$_3$ was prepared by atomic layer deposition (ALD) technology. Trimethyl Aluminum (TMA) and H$_2$O were used as precursors for the ALD of Al$_2$O$_3$ layer at 150 °C. Leakage current—voltage characteristics were assessed using a B1500A semiconductor device analyzer.

3. Discussion

The effect of ODT passivation on the bonding chemistry of GaAs was examined by collecting As 3d and Ga 2p spectra. Figure 1a shows the As 3d XPS spectra of the unpassivated and ODT passivated samples. It is clear that the As 3d spectra of the unpassivated sample overlapped with three fitted subpeaks: 40.87 eV, 41.56 eV and 44.37 eV, respectively. The peaks at 40.87 eV and 41.56 eV corresponded to the As 3d5 bond and As 3d3 bond in GaAs bulk, while the peak at 44.37 eV corresponded to As$_2$O$_3$, which was obvious after HF immersion. After ODT passivation, we observed an absolute removal of the As$_2$O$_3$ bond and an additional formation of an As-S (42.24 eV) bond. Inset of Figure 1a represents the S 2p spectrum, which also indicates an evident sulfur layer on the GaAs wafer.
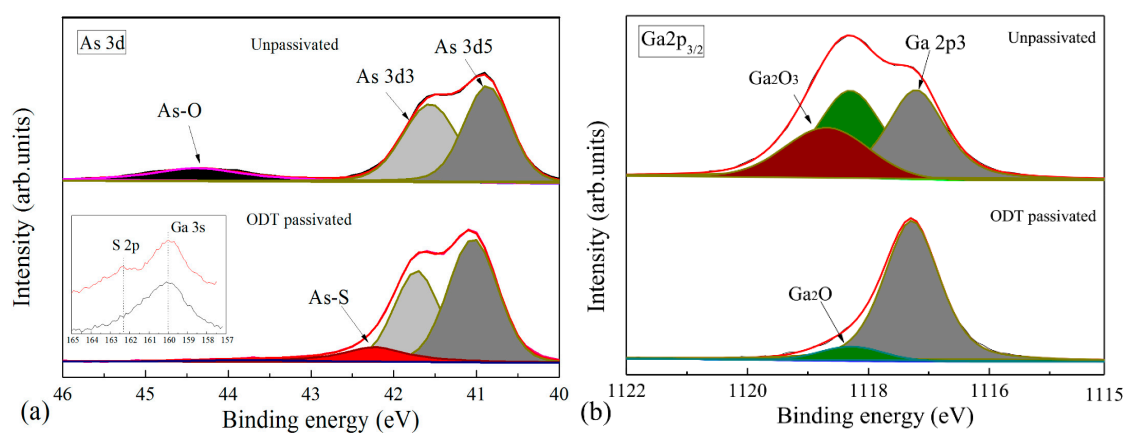

Figure 1. (**a**) As 3d (**b**) Ga 2p3/2 XPS spectra of unpassivated and ODT treated GaAs surface.

Ga 2p spectra is extremely surface sensitive. In the case of the Ga 2p$_{3/2}$ XPS spectra, shown in Figure 1b, three distinctive subpeaks were identified: Ga-As (1117.15 eV), Ga$_2$O (1118.25 eV), Ga$_2$O$_3$

(1118.64 eV). After ODT passivation, the Ga_2O_3 peak was removed and the Ga_2O peak dramatically decreased. Different from the formulation of the As-S bond, the examination of the Ga-S bond was difficult because of the similar binding energy between the Ga-S bond and Ga-O bond. This is consistent with the report by Pablo Mancheno-Posso [13]. The XPS comparison confirms the effectiveness of the ODT passivation for the removal of the As oxides and most Ga oxides.

In order to further demonstrate the effect of ODT passivation, especially the stability of air exposure, we prepared three groups of samples for Raman spectral analysis: unpassivated, ODT passivated and exposure in air for 3 days after ODT passivation respectively, as shown in Figure 2a–c. The longitudinal-optic-phonon-plasmon coupled (LOPC) mode near 265 cm^{-1} is from GaAs body material, and the longitudinal optic (LO) mode at 288 cm^{-1} is from the surface depletion layer. When there is a high state density on the GaAs surface, the LO mode will be measured. When the excited light penetrates deeper than the thickness of the depletion layer, LOPC mode will be measured. Therefore, an effective passivation can cause a decrease in the LO peak intensity and an increase of the LOPC peak intensity [15–17].
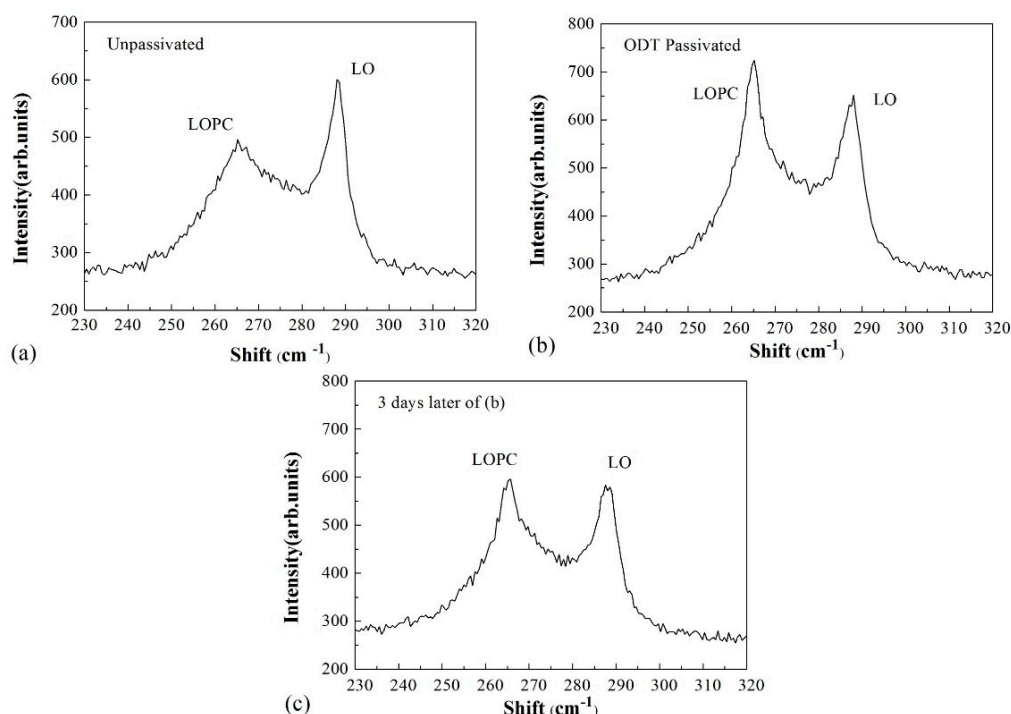
Figure 2. Raman spectra of GaAs (100) surface (**a**) unpassivated, (**b**) ODT passivated, (**c**) exposure in air for 3 days after ODT passivated.

It can be seen from Figure 2 that the passivation changed the balance between the LOPC (265 cm^{-1}) peak and the LO (288 cm^{-1}) peak. For the unpassivated GaAs surface in Figure 2a, the ratio of peak intensity I_{LOPC}/I_{LO} is 0.826, which means the original surface state density was relatively high. After ODT passivation for 24 h at room temperature, the intensity of LOPC peak increased considerably indicating that the surface state density was significantly reduced, and the ratio of peak intensity I_{LOPC}/I_{LO} is 1.110 in Figure 2b.

Figure 2c shows the Raman spectra of the sample placed in the air for 3 days after being passivated by ODT. It was clear that the LOPC peak was only slightly reduced compared with Figure 2b, we also found that the degradation rate of ODT passivation in the N_2 atmosphere was nearly zero in 24 h (data not shown). Thus, ODT SAMs provide a good surface protection that may allow the integration of such process into GaAs semiconductor device manufacture

The GaAs surface covered with native oxide layer is the origin of the high surface state density, pinning the surface Fermi level within the band gap of semiconductor. So, the radiative transition

is weak when the surface state density is high. The PL intensity which indicates a radiative transition band-to-band will increase when there is a decrease of state density on the GaAs surface after passivation.

The immersion time has a significant influence on the passivation effect [18], thus PL spectra was recorded at room temperature for 4 h, 8 h, 16 h, 24 h, 36 h and 48 h ODT immersion. As shown in Figure 3, the PL intensity kept a continuous enhancement as time extended in the range of 0–24 h, which is related to the reduced oxygen contamination and the increased density of ODT molecules in the SAM. Longer ODT immersion than 24 h did not further improve the PL intensity obviously, and the maximum PL enhancement was 116%.
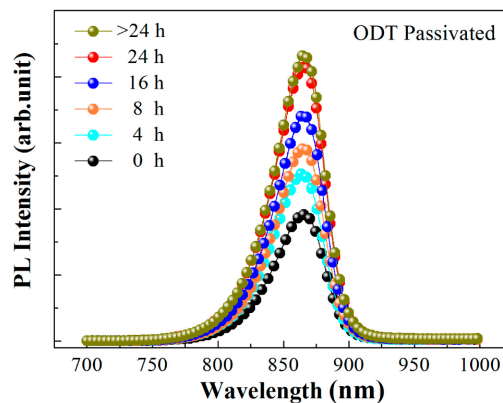
Figure 3. PL spectra of GaAs (100) surface after ODT passivation for different times.

Some surface treatment, such as plasma or acid immersion, can remove native oxides but are most likely to result in a poor surface morphology, which is harmful to subsequent device preparation. Figure 4 shows the SEM image of the GaAs (100) surface before and after ODT passivation, here the GaAs surface was pre-sprayed with Pt thin film to enhance the conductivity. It is clear that, the unpassivated surface had a poor surface morphology due to the thick native oxide layer, and a better uniform surface was achieved after ODT passivation. It is related to ODT passivation removing the native oxide and forming a regular SAMs on the surface.
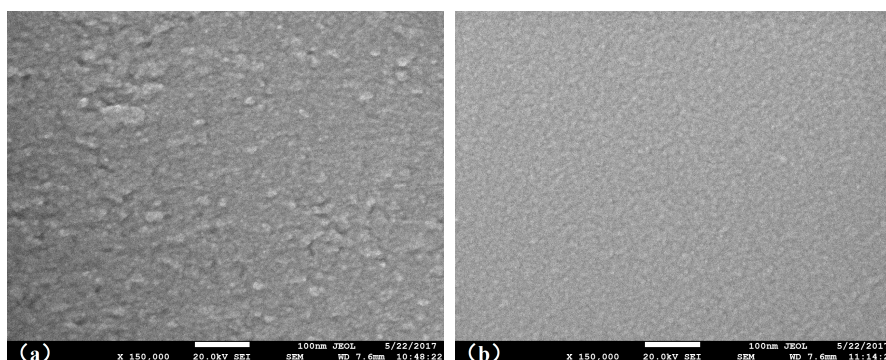
Figure 4. Contrast SEM image of GaAs surface (**a**) unpassivated (**b**) ODT passivated. The scale bar of both SEM images is 100 nm.

Electrical measurement was performed on metal-oxide-semiconductor capacitors. Figure 5 shows the leakage current—voltage curve of $Al/Al_2O_3/GaAs$-MOSCAP before and after ODT passivation at room temperature. The Al_2O_3 was obtained by an ALD method, obtaining a final thickness of 10 nm. It can be seen that after the ODT passivation, the device gate leakage current significantly decreased, indicating the decreased interface defects between the GaAs and the dielectric layer.
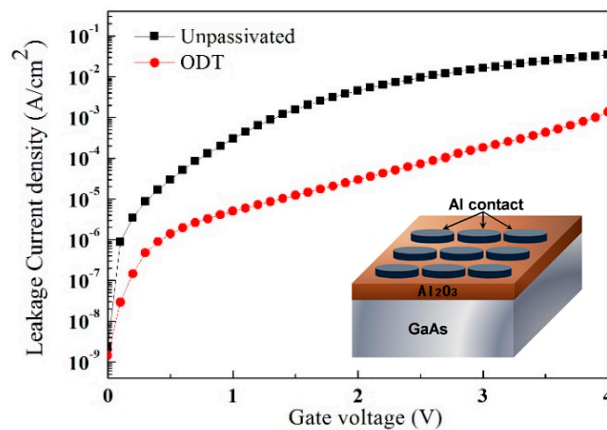
Figure 5. Leakage current density curve of Al/Al$_2$O$_3$/GaAs-MOSCAP.

4. Conclusions

In summary, sulfur passivation of ODT SAMs was performed on GaAs (100) wafers. It is able to remove native oxides and shows a good surface morphology, meanwhile the ODT SAMs appears to be more stable in air exposure. PL intensity shows a continuous enhancement with passivation time, extending in the range of 0–24 h, and the maximum PL enhancement was 116%. The passivation processes uses ethanol as the only solvent and produces less sulfide volatilization, which is efficient and environmentally friendly.

Author Contributions: L.Z. designed the experiment and wrote the manuscript; X.C. performed measurements and analyzed data; Y.C. supervised and managed the project; X.Y. designed the experiment and edited the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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