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In situ passivation of InP surface using H₂S during metal organic vapor phase epitaxy

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An *in situ* surface passivation of InP(100) using H_2S during metal organic vapor phase epitaxy has been characterized by x-ray photoemission spectroscopy and photoluminescence. X-ray photoelectron spectra indicate that the H_2S -treated InP at 300 °C is free of P and In oxides even after exposure to air. The enhancement of photoluminescence intensity confirms that H_2S passivation of an InP epilayer can reduce the surface defects. It is shown that H_2S treatment results in In–S bonds, which dominate the sulfur-passivated InP surface, effectively suppressing interface oxidation during the subsequent ultrathin Al_2O_3 dielectric film growth. © 2009 American Institute of Physics. [doi:10.1063/1.3233935]

Recently, there has been a renewed research interest in III-V semiconductor materials as alternative channel material other than Si in metal oxide semiconductor field effect transistors (MOSFETs), and their applications at the 22 nm feature size and beyond due to intrinsic transport properties.¹⁻⁵ However, preparations of well-defined III-V surfaces and high-quality oxide-semiconductor interfaces with low interface state density remain challenging tasks. Some encouraging results have been reported in the refinement of III-V MOSFETs technology including in situ deposition of Ga₂O₃ (Gd_2O_3) ,⁶ molecular beam epitaxy of Gd_2O_3 ,⁷ and atomic layer deposition of Al₂O₃ (Refs. 1 and 8) and HfO₂ (Ref. 3) thin films on GaAs or InGaAs. Similarly, InP inversion-type MOSFETs with atomic layer deposition Al₂O₃ have demonstrated the capability of high drive current density, and can provide a much smaller off-current density compared to InGaAs.⁹ In addition, the insulated gate structure of an InP MOSFET allows the larger gate-voltage swing in both po-larities needed in high power devices.¹⁰ However, InP compounds do not have native oxides suitable for use as insulators in MOSFETs. Thus, an externally applied insulator, and a method for applying it is required. Compounds of SiO₂, Al_2O_3 , and Si_3N_4 have been previously employed to produce insulated gate layers on InP.¹¹ More recently, InP-based MOS structures with HfO2 grown by atomic layer deposition have also been prepared by Kim et al.¹²

Prior to insulator deposition, the InP surface should be pretreated and well passivated, as InP rapidly oxidizes in air to form a native oxide around 1–2 nm thick. In the absence of special precautions to eliminate native oxide formation, prior to deposition of a dielectric layer, it is likely that the electrical properties of the interface will be greatly affected by the native surface oxide. As a result, many surface treat-

ment methods have been proposed to improve InP surface properties before dielectric deposition. One method employs aqueous sulfur solutions such as S₂Cl₂ and (NH₄)₂S solutions to passivate the substrate surface with a sulfur layer.¹³ It was reported that applying sulfur passivation using (NH₄)₂S and postdeposition annealing improve the drive current and subthreshold swing.¹⁴ While there have been remarkable improvements in surface recombination velocity and device performance, some problems still exist such as poor reproducibility and aging effects. Another method employing H₂S in an ultrahigh vacuum chamber has been demonstrated to produce higher quality device surfaces, than those treated with the wet process.¹⁵ Passivation of the electronic defect states at the SiN_r/InP interface has been achieved by Kaplia et al.¹¹ using gaseous H₂S treatments of the InP surface. Despite considerable experimental and theoretical work, the atomic structures of sulfur treated III-V surfaces are not established and the passivation mechanism is still unclear.

In this work, an *in situ* passivation of InP(100) surface with H₂S during metal organic vapor phase epitaxy (MOVPE) has been chosen to prevent the formation of native oxides and suppress the interfacial oxide growth during the dielectric Al₂O₃ growth. The chemical and structural properties of *in situ* H₂S treated InP(100) surfaces, and surfaces capped with an ultrathin Al₂O₃ layer are reported.

The InP epitaxial layers were grown on a S-doped *n*-InP(100) wafer using a horizontal MOVPE reactor (AIX-TRON, AIX200/4). During the epitaxial growth process, trimethy-indium and tertiarybutyl-phosphine were selected as the sources of In and P, respectively. All specimens were prepared at 600 °C using a hydrogen carrier flow with a growth pressure of 10 kPa. After the growth of InP epilayers, sulfur passivation was performed using hydrogen sulfide (H₂S) in the temperature range of 200–350 °C for 30 min in the MOVPE reactor. After surface treatment, a 3 nm Al₂O₃

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FIG. 1. (Color online) XPS data of (a) P 2p and (b) In 3d spectra for as-received, epitaxial, H2S-treated InP surfaces.

film as measured by spectroscopic ellipsometry was deposited by metal-organic chemical vapor deposition at 300 °C using dimethylaluminumhydride and O_2 as precursors.

The specimens were then transfered into an ultrahigh vacuum x-ray photoemission spectroscopy (XPS) chamber in less than 15 min. The XPS measurements were performed in an ULVAC-PHI Model 1600C system equipped with a nonmonochromatic Mg $K\alpha$ (1253.6 eV) line as an x-ray source. All experiments were conducted at 2.7×10^{-7} Pa. Photoelectrons were taken from the surface with 45° angle, and the C 1s peak at 284.6 eV was taken as a reference for charge correction. Photoluminescence (PL) data was collected at room temperature under excitation by an argon ion laser beam of 514.5 nm.

The chemical binding states of InP samples prior to the Al_2O_3 deposition were first investigated by XPS. P 2p and In 3d core levels for the samples with and without H₂S treatments are shown in Fig. 1. The P 2p core level spectrum attributed to the P-In bond from the substrate is composed of two peaks, P $2p_{1/2}$ (129.3 eV) and P $2p_{3/2}$ (128.5 eV), as shown in Fig. 1(a). A component at higher binding energy with a peak at 133.1 eV which correlates with a P-O bond was observed for the as-received sample, conducive with the presence of P oxide on the surface of the sample.¹⁶ A small amount of P oxide also exists in the InP epilayer surface. However, the peak with a binding energy in the vicinity of 133 eV was not observed in the XPS spectra of H₂S-treated InP surface, suggesting that neither P-O nor P-S bond $(\sim 132.6 \text{ eV})$ (Ref. 17) exists on the H₂S treated InP surface.

When considering the In 3d spectra, only the In $3d_{5/2}$ peaks will be addressed for simplicity, which are presented in Fig. 1(b). The In $3d_{5/2}$ features can be deconvoluted into three binding energy regions, which are assigned to In-O, In-S, and In-P species, respectively. The peak arising at 444.3 eV is due to In–P bonding.¹⁸ Although the distinction between O and S bonding to In is difficult to establish from XPS spectra information alone, there is a measurable difference which suggests a distinction. The binding energy of In–O peak is slightly higher than that for the In–S peak with peaks at 444.9 and 445.1 eV originating from In-S and In-O bonds, respectively. It also can be seen that the In-S component increases with increased H₂S treatment temperature from 200 to 300 °C while the In-O component decreases. The In oxides presence for the H₂S-treated sample at 300 °C was negligible. However, it shall be noted that the amount of In-S decreases for the sample treated at 350 °C. This phenomenon may be due to partial desorption of S from the This a sample surface. Based on the information from P 2p and In



FIG. 2. (Color online) O 1s core level spectra for as-received, epitaxial, H₂S-treated InP surfaces. Inset shows the deconvolution of O 1s signal for as-received and epitaxial InP surfaces.

3d spectra, it is concluded that the H₂S treated InP surface is terminated by In-S bonds, which can protect the InP surface from oxidation during exposure to air.

Figure 2 shows the O 1s core level spectra for the asreceived, epitaxial, and H₂S treated samples. The O 1s peaks for as-received and epitaxial samples (inset to Fig. 2) could be split into two components, O-P (531.7 eV) and O-In (531.1 eV), respectively. It can be observed that the intensity of O-P signal for epilayer decreases compared to that for as-received sample. These results are in agreement with the P 2p spectra deconvolution. Moreover, the intensity of O 1s peak for H₂S-treated samples is much lower than that for as-received and epitaxial samples. The minor oxygen in the sulfide passivated samples is believed from the adsorbed surface CO₂ (531.0 eV). Based on the above In $3d_{5/2}$ spectra information, it suggests that the sulfur can bridge between the surface In atoms through occupying the P-related vacancies. As a result, the surface would be passivated as there would be practically no dangling bonds on the sulfurpassivated InP surface.

A qualitative indication of passivation can be achieved by comparing the PL intensity, which is related to the electrical properties of MOS capacitor.¹⁹ The PL spectra of InP samples before and after H₂S treatments are shown in Fig. 3. The spectra show a broadband with an intense peak at 1.37 eV due to transitions from band to band.²⁰ This peak is slightly above the intrinsic bandgap energy ($E_{go}=1.35$ eV) of n-InP. As can be seen, a clear enhancement of the PL intensity is observed for the epitaxial and H₂S-treated samples. It is reported that the PL intensity varies with the amount of oxide formed on InP surface and surface defects.¹⁶ The increase in PL intensity for the epitaxial InP sample compared to the as-received one suggests that only a small amount of native oxide was present on its surface. The further increase in PL intensity for the H₂S treated samples was due to not only the decrease in native oxides but also the reduction in surface recombination velocity caused by the reduction in surface state density.¹⁶ As a result, the surface defects acting as interface traps were nearly passivated after an $in_1situ_1H_2S_1$ treatmentation.aip.org/termsconditions. Downloaded to IP:



FIG. 3. (Color online) PL spectra of as-received, epitaxial, H₂S-treated InP(001) samples. The dashed line identifies the intrinsic bandgap energy (E_{go}) of *n*-InP.

Figure 4 shows the XPS data of InP(001) surfaces with and without H₂S treatment followed by 3 nm deposition of Al₂O₃. It can be seen clearly from Fig. 4(a) that the presence of strong P–O bonds for the epitaxial sample. On the contrary, for the sulfur-passivated sample at 200 °C, the P–O peak intensity significantly reduced. P–O bonds were not de-



FIG. 4. (Color online) XPS data of (a) P 2p and (b) In 3d spectra for as-received, epitaxial, H₂S-treated InP surfaces after 3 nm Al₂O₃ deposition.

tected in sulfur-passivated samples at 300 °C, indicating that H_2S passivates the InP surface and, therefore, inhibiting the interfacial oxide regrowth during Al_2O_3 deposition. It is also noted that a certain amount of indium oxide exists at the top of InP epitaxial surface, as suggested by the slight shift of peak position to higher energy (~0.2 eV). There was no increase in indium oxides [Fig. 4(b)] after thin Al_2O_3 films grown on sulfur-passivated InP sample, indicating the good stability of the sulfur-passivated InP sample.

In summary, XPS and PL have been employed to characterize the chemical and structural properties of *in situ* S-passivated InP surface using H₂S. The P and In oxides were not observed for the H₂S-treated InP epitaxial sample at 300 °C. The enhancement of photoluminescence intensity after H₂S treatment was attributed to the decrease in native oxides and surface defects. The regrowth of In or P oxides on the sulfur-passivated InP sample during the subsequent Al₂O₃ deposition was effectively suppressed. It is concluded that the H₂S treatment at 300 °C was effective in preventing the formation of native oxides and inhibiting interfacial oxide regrowth.

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