

# Low Interface State Density of Liquid-Phase-Deposited $SiO_2$ Films on $(NH_4)_2S_x$ -Treated InP

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The electrical characteristics, including current-voltage, capacitance-voltage, hysteresis loops, and interface state density, of liquid-phase-deposited (LPD)-SiO<sub>2</sub> grown on p-type (100) indium phosphide substrates with and without  $(NH_4)_2S_x$  treatments were investigated. The aqueous solution of hydrofluosilicic acid and boric acid were used as the growth solution for silicon dioxide films. The indium phosphide with ammonium sulfide treatment improves the electrical characteristics. The electrical characteristics depend on the boric acid concentration in the growth solution. The leakage currents can reach 6.24 and  $8.14 \times 10^{-8}$  A/cm<sup>2</sup> under positive and negative electric fields at 0.5 MV/cm. The effective oxide charges are  $-5.33 \times 10^{10}$  C/cm<sup>2</sup>. The interface state density is 9.65  $\times 10^{10}$  cm<sup>-2</sup> eV<sup>-1</sup> at the energy of 0.67 eV from the valance band. © 2007 The Electrochemical Society. [DOI: 10.1149/1.2772095] All rights reserved.

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Due to the high electron mobility and direct energy bandgap compared with Si, much attention has been focused on InP highspeed and optoelectronic devices. The metal-semiconductor fieldeffect-transistor (MESFET) is the one of the main structures. Compared with the metal-oxide-semiconductor field-effect-transistor (MOSFET), the main disadvantage of MESFET is the high gate current of Schottky contact under the forward bias of several tenths of a volt due to the lack of stable and high-quality oxide on it. It severely limits the maximum drain current, the noise margin, and the flexibility of the circuit design. The gate-insulating layer of MOSFET can improve those disadvantages.

The high density of interface states is the major problem of III-V compound semiconductor MOSFET, which causes the pinning of the surface Fermi level near the middle of the energy gap.<sup>1</sup> From previous studies,<sup>2,3</sup>  $(NH_4)_2S_x$  treatment can prevent InP from oxidizing after cleaning and the chemically bonded In-S species can be formed on InP surface to assist the top InP layer in reconstructing its crystalline structure. Usually, traditional silicon oxide growth methods like chemical vapor deposition (CVD) and plasma-enhanced CVD (PECVD) were used for MOS fabrication. From previous studies, the  $(NH_4)_2S_x$  passivation degrades as the temperature raises higher than 250°C for GaAs substrate.<sup>4</sup> InP has similar properties for  $(NH_4)_2S_x$  passivation.<sup>5,6</sup> Liquid-phase deposition (LPD) has many advantages such as low-temperature deposition (room temperature is permissible), uniformity, selectivity, and low cost.<sup>7</sup> The low growth temperature of LPD-SiO<sub>2</sub> on (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub>-treated InP  $(\mbox{LPD-SiO}_2/\mbox{S-InP})$  can preserve the passivation function of  $(NH_4)_2S_x$  treatment. In this study, the electric characteristics of LPD-SiO<sub>2</sub> grown on InP substrate without and with  $(NH_4)_2S_x$  treatments were investigated.

### Experimental

Zn-doped p-type InP(100) with carrier concentration of  $2 \times 10^{16}$  cm<sup>-3</sup> was used as the substrate in this study. InP substrate was degreased in solvent, followed by chemical etching in a solution (H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O = 5:1:1) for 3 min, and then rinsed in deionized water. For (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub> treatment, InP substrate was dipped into (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub> solution for 16 h at room temperature after cleaning and then blown dry with nitrogen gas.<sup>8</sup> In order to speed the In–S bond formation on InP surface, the treatment temperature is raised to 50°C and the treatment time is shortened to 40 min in this study.<sup>9,10</sup> After (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub> treatment, the InP substrate was thermally annealed at 220°C in a nitrogen atmosphere for 10 min to desorb the excess of weakly bonded sulfide,<sup>11</sup> and the InP substrate with (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub>

treatment is ready for LPD–SiO<sub>2</sub> deposition. Without the thermal treatment, the electrical properties of LPD–SiO<sub>2</sub>/S–InP are poor due to the excess of sulfur at the interface.<sup>2</sup>

The LPD deposition system contains (*i*) a temperature-controlled water bath offering a uniform deposition temperature with the accuracy of  $\pm 0.1$  °C and (*ii*) a Teflon vessel which contains the deposition solution, in which hydrofluosilicic acid (H<sub>2</sub>SiF<sub>6</sub>, 3.8 M) aqueous solution saturated with silica-gel (silicon dioxide gel) and boric acid (H<sub>3</sub>BO<sub>3</sub>) aqueous solution (0.01 M) were used as the precursors.

Scanning electron microscopy (SEM) was used to examine the thickness. The refractive index *n* of SiO<sub>2</sub> film was measured by spectroscopic reflectance meter. A MOS structure was used to examine the electrical characteristics. In (10%)–Zn (90%) alloy was evaporated on InP bottom for ohmic contact and then thermally annealed at 400°C in a nitrogen atmosphere for 3 min. Al was used as the top contact with the area of  $7.07 \times 10^{-4}$  cm<sup>2</sup>. A HP4145B semiconductor-parameter analyzer was used for current-voltage (*I-V*) characterization. A high-frequency (1 MHz) HP4280A capacitance-voltage (*C-V*) meter was used for *C-V* characterization scanned from accumulation region to inversion region. The interface state density was derived from the *C-V* curve by the Terman method.<sup>12-15</sup> The quasistatic *C-V* measurement was measured by HP 4156. The dc bias was swept by 1/20 V/s and can provide a sufficiently accurate value of interface state densities ( $D_{it}$ ).<sup>16,17</sup>

#### **Results and Discussion**

In this study, the volume of H<sub>2</sub>SiF<sub>6</sub> aqueous solution is kept at 32 mL and mixed with H<sub>3</sub>BO<sub>3</sub> aqueous solution of 15, 25, and 35 mL, respectively. The deposition temperature was kept at 40°C for 30 min. The corresponding thickness is 68, 101, and 147 nm, respectively. The growth rate and thickness of LPD-SiO<sub>2</sub>/S-InP as a function of H<sub>3</sub>BO<sub>3</sub> volume was shown in Fig. 1. Basically, the growth rate of LPD-SiO<sub>2</sub> film increases with H<sub>3</sub>BO<sub>3</sub> volume. It is from this that the hydrofluoric acid (HF) neutralization increases with  $H_3BO_3$  volume and drives higher saturation of  $SiO_2$  in the growth solution and therefore higher growth rate.<sup>18</sup> The refractive indexes are 1.39, 1.41, and 1.22 for H3BO3 15, 25, and 35 mL, respectively. The slightly lower refractive index than that of thermal silicon dioxide could be from a high concentration of F for H<sub>3</sub>BO<sub>3</sub> 15 and 25 mL. For H<sub>3</sub>BO<sub>3</sub> 35 mL, the lower refractive index is from the high growth rate. The SEM cross section of LPD-SiO<sub>2</sub>/S-InP at the volume of H<sub>3</sub>BO<sub>3</sub> 25 mL is shown in Fig. 2. The high quality of LPD-SiO<sub>2</sub> film and good interface of LPD-SiO<sub>2</sub> and InP can be observed in the figure.

Figure 3 shows the *I-V* characteristics of LPD–SiO<sub>2</sub>/InP and LPD-SiO<sub>2</sub>/S-InP as a function of H<sub>3</sub>BO<sub>3</sub> volume. The leakage current is sensitive to H<sub>3</sub>BO<sub>3</sub> volume. For the LPD-SiO<sub>2</sub>/InP, the leakage currents are  $4.3 \times 10^{-5}$  and  $1.71 \times 10^{-3}$  A/cm<sup>2</sup> for the H<sub>3</sub>BO<sub>3</sub>

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Figure 1. Growth rate and thickness of LPD-SiO\_/S–InP as a function of  $\rm H_{3}BO_{3}$  volume.

volume of 15 mL and  $2.07 \times 10^{-6}$  and  $4.7 \times 10^{-5}$  A/cm<sup>2</sup> for the H<sub>3</sub>BO<sub>3</sub> volume of 25 mL under positive and negative electric fields at 0.5 MV/cm as shown in Fig. 3a and b, respectively. The lower H<sub>3</sub>BO<sub>3</sub> volume results in higher F concentration in the solution. The excessive F atom can substitute the oxygens in Si–O–Si bonds to form Si–F and release nonbridged oxygen centers of atomic group O–Si and form traps in the film and at the interface,<sup>19</sup> which are responsible for the higher leakage current. For the H<sub>3</sub>BO<sub>3</sub> volume of 35 mL, the leakage currents become much higher and are 6.63  $\times 10^{-2}$  and 3.32  $\times 10^{-1}$  A/cm<sup>2</sup> under positive and negative electric fields at 0.5 MV/cm as shown in Fig. 3c. SiO<sub>2</sub> is precipitated in the solution due to a too-high H<sub>3</sub>BO<sub>3</sub> volume. The inferior quality is from the incorporation of SiO<sub>2</sub> precipitation in the film and the higher deposition rate. Therefore, the optimum H<sub>3</sub>BO<sub>3</sub> volume is 25 mL due to the proper F concentration and the growth rate.

Due to higher interface and film quality by the native oxide removal and the reconstruction of InP surface after  $(NH_4)_2S_x$  passivation,<sup>3</sup> the leakage currents of the LPD-SiO<sub>2</sub>/S–InP are much improved. The optimum H<sub>3</sub>BO<sub>3</sub> volume is still 25 mL. For the H<sub>3</sub>BO<sub>3</sub> volume of 25 mL, the leakage currents can reach 6.24 and  $8.14 \times 10^{-8}$  A/cm<sup>2</sup> under positive and negative electric fields at 0.5 MV/cm as shown in Fig. 3e. The trends are similar to that of LPD-SiO<sub>2</sub>/InP.

The C-V characteristics of LPD-SiO<sub>2</sub>/InP and LPD-SiO<sub>2</sub>/S–InP as a function of the  $H_3BO_3$  volume are shown in Fig. 4. The LPD-SiO<sub>2</sub>/InP with  $H_3BO_3$  volume of 15 mL shows a serious stretch-out phenomenon in the accumulation region as shown in Fig. 4a. This stretch-out phenomenon is associated with the interface



Figure 3. *I-V* characteristics of LPD-SiO<sub>2</sub>/InP and LPD-SiO<sub>2</sub>/S–InP as a function of  $H_3BO_3$  volume.

traps by the excessive F at the LPD-SiO2/InP interface.<sup>19</sup> For the H<sub>3</sub>BO<sub>3</sub> volume of 25 mL, the slight stretch-out phenomenon is much improved due to better interface quality as shown in Fig. 4b. For the H<sub>3</sub>BO<sub>3</sub> volume of 35 mL as shown in Fig. 4c, the decay of the accumulation capacitance results from the high leakage current due to inferior film quality as mentioned above. For LPD-SiO<sub>2</sub>/S-InP, sharper C-V curves are obtained. For the H<sub>3</sub>BO<sub>3</sub> volume of 15 mL, the C-V curve is shown in Fig. 4d. The stretch-out phenomenon of the C-V curve is associated with the defects at the LPD-SiO<sub>2</sub>/S-InP interface from the destruction of the passivation function of  $(NH_4)_2S_x$  treatment by higher HF concentration in the solution but is improved due to  $(NH_4)_2S_x$  treatment compared with that in Fig. 4a. For the H<sub>3</sub>BO<sub>3</sub> volumes of 25 mL, the stretch-out phenomenon in the accumulation region is not observed due to the passivation function of  $(NH_4)_2S_x$  treatment for lower HF concentration as shown in Fig. 4e. For the H<sub>3</sub>BO<sub>3</sub> volume of 35 mL as shown in Fig. 4f, the decay of the accumulation capacitance is from the high leakage current as shown in Fig. 3f. All curves show the deep depletion phenomenon, which is from the lower generation rate of minority electron carrier of InP.<sup>14,20,21</sup> The dielectric constant  $\epsilon_{ox}$  of



Figure 2. SEM cross section of LPD-SiO\_2/S–InP at the volume of  $\rm H_{3}BO_{3}$  25 mL.



Figure 4. C-V characteristics of LPD-SiO\_2/InP and LPD-SiO\_2/S–InP as a function of  $\rm H_3BO_3$  volume.



Figure 5. Hysteresis loops of LPD-SiO<sub>2</sub>/S–InP for the  $H_3BO_3$  volume of (a) 15, (b) 25, and (c) 35 mL.

LPD-SiO<sub>2</sub>/S–InP with  $H_3BO_3$  volume 15, 25, and 35 mL are 3.32, 3.81, and 3.63, respectively. This indicates that the stoichiometry of LPD-SiO<sub>2</sub> for  $H_3BO_3$  volume 25 is close to the ideal SiO<sub>2</sub>.

The hysteresis loops of LPD–SiO<sub>2</sub>/S–InP with the  $H_3BO_3$  volume of 15, 25, and 35 mL are shown in Fig. 5a-c, respectively. For *C-V* measurement, the bias scans from the accumulation region to



Figure 6. Interface state densities of LPD-SiO<sub>2</sub>/S–InP as a function of the  $H_3BO_3$  volume and PL measurement (inset).

the inversion region (forward scan) and then back to the accumulation region (backward scan). The flatband voltage shift is defined as the difference of the flatband voltage between the forward scan and the backward scan. The flatband voltage shifts are 0.09, 0.04, and 0.16 V. They indicate that the amount of traps in the oxide films are small<sup>13</sup> and the trend is the same as  $D_{\rm it}$ .

The D<sub>it</sub> of LPD-SiO<sub>2</sub>/S-InP as a function of H<sub>3</sub>BO<sub>3</sub> volume derived from the Terman method are shown in Fig. 6. The  $D_{it}$  are  $8.33 \times 10^{11}$ ,  $9.65 \times 10^{10}$ , and  $4.92 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$  for the  $\rm H_{3}BO_{3}$  volume of 15, 25, and 35 mL at the energy of 0.67 eV from the edge of the valence band. The lowest  $D_{it}$  and  $Q_{eff}$  for the H<sub>3</sub>BO<sub>3</sub> volume of 25 mL is from the suitable HF etching and the best interface passivation by  $(NH_4)_2S_r$  treatment. The photoluminescence (PL) spectra of InP and S-InP are also shown in the inset of Fig. 6. The lower PL intensity for InP without  $(NH_4)_2S_x$  treatment shows a high surface recombination velocity.<sup>22,23</sup> The PL intensity is much improved for InP with  $(NH_4)_2S_x$  treatment. This indicates that the  $(NH_4)_2S_x$  passivation is an effective way to reduce the surface recombination velocity.<sup>24</sup> In order to double check the  $D_{it}$ , the highlow frequency capacitance (HLCV) method was used. The HLCV curves for the H<sub>3</sub>BO<sub>3</sub> volumes of 15, 25, and 35 mL are shown in Fig. 7a-c, respectively. The lowest  $D_{it}$  derived from HLCV are  $6.03 \times 10^{11}$ ,  $9.93 \times 10^{10}$ , and  $4.61 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$  for the H<sub>3</sub>BO<sub>3</sub> volumes of 15, 25, and 35 mL. The comparison of the lowest D<sub>it</sub> derived by Terman and HLCV methods is shown in Fig. 8. Two measurement methods show almost the same results.

# Conclusion

LPD-SiO<sub>2</sub> films grown on p-type InP(100) substrate with and without (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub> treatment were investigated. The LPD-SiO<sub>2</sub>/InP shows poor electrical characteristics. The *I-V* and *C-V* characteristics are much improved for LPD-SiO<sub>2</sub>/S–InP. For the H<sub>3</sub>BO<sub>3</sub> volume of 25 mL, optimized electrical characteristics can be obtained due to the proper deposition rate and the best (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub> passivation. The leakage currents are 6.24 and 8.14 × 10<sup>-8</sup> A/cm<sup>2</sup> under positive and negative electric fields at 0.5 MV/cm. The  $Q_{\rm eff}$  is -5.33 × 10<sup>10</sup> C/cm<sup>2</sup> and the  $D_{\rm it}$  is 9.65 × 10<sup>10</sup> cm<sup>-2</sup> eV<sup>-1</sup> at the energy of 0.67 eV from the valance band.

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Figure 7. HLCV curves for the  $\rm H_3BO_3$  volume of (a) 15, (b) 25, and (c) 35 mL.



**Figure 8.** Comparison of lowest  $D_{it}$  as a function of the H<sub>3</sub>BO<sub>3</sub> volume derived by Terman and HLCV methods.

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