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Electrical characteristics of $TiO_2/Al_2O_3/InP$ capacitor after removal of native oxides by atomic layer deposited Al_2O_3 self-cleaning and $(NH_4)_2S$ treatments

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ABSTRACT

The electrical characteristics of MOS capacitor with 5/2.9 nm TiO_2/Al_2O_3 prepared by atomic layer deposition on $(NH_4)_2S$ treated InP were studied. The electrical characteristics were improved from the reduction of native oxides and sulfur passivation on InP by $(NH_4)_2S$ treatment. The high dielectric constant TiO_2 is used to lower the equivalent oxide thickness and the atomic force microscopy image reveals extremely flat and uniform surface. The root-mean-square roughness value of TiO_2/S-InP is 0.226 nm. The stack of high bandgap Al_2O_3 layer can reduce the thermionic emission of low bandgap TiO_2 and its self-cleaning capability further improves the interface state density. For 5/2.9 nm TiO_2/Al_2O_3/S-InP stacked MOS capacitor, the leakage currents can reach 6.4×10^{-8} and 7.8×10^{-7} A/cm^2 at ± 2 MV/cm, respectively. The net effective dielectric constant is 16.7. The lowest interface state density is 3.8×10^{11} $cm^{-2}eV^{-1}$ with a low frequency dispersion of 16%.

1. Introduction

Owing to higher electron mobility compared with Si, much attention has been focused on indium phosphide (InP) high-speed devices. Currently, the metal–semiconductor field effect transistor (MESFET) is the main structure of InP high-speed devices due to the lack of a stable and high quality oxide on it. The main disadvantage of MESFET is the high leakage current of Schottky gate under the positive bias of several tenths of a volt, and severely limits the maximum drain current, the noise margin and the flexibility of the circuit design. Compared with MESFET, the gate insulating layer of metal–oxide–semiconductor field effect transistor (MOSFET) can improve these disadvantages. Many high-*k* dielectrics, such as TiO_2 [1], $LaAlO_3$ [2], Al_2O_3 [3], and HfO_2 [4] are currently being explored on InP, and the thicker gate materials with the same gate capacitance per unit area can result in less carrier tunneling and hence the leakage current. Among various high-*k* materials, TiO_2 with larger dielectric constant (*k* value 4–86) [5] and lower equivalent oxide thickness (EOT) can be obtained. However, high interface state density (D_{it}) mainly contributed by native oxides [6] and high thermionic emission leakage current due to low bandgap TiO_2 (3.5 eV) [7] are problems.

Usually, high D_{it} is a major concern in the development of III–V compound semiconductor MOSFETs [8,9]. The removal of native oxides at the high-*k*/InP interface is therefore a key factor for achieving high performance MOSFETs [10]. It was reported that the $(NH_4)_2S$ solution can reduce the surface oxides on InP [11–13] and cover the surface with sulfur atoms to prevent further oxidization [14,15]. This technique has been applied to device fabrication and clearly shows the improved electrical properties [13]. However, a previous study shows that the $(NH_4)_2S$ solution cannot remove the native oxides completely [16]. Al_2O_3 prepared by atomic layer deposition (ALD) has a surface self-cleaning reaction to consume native oxides on III–V compound semiconductors due to ALD chemistry [10,17]. Moreover, Al_2O_3 has a high bandgap (9 eV), high breakdown electric field (5–10 MV/cm), high *k* constant (8.6–10), and high thermal stability up to at least 1000 °C, and remains amorphous under typical processing conditions [18]. Al_2O_3 is a widely used insulator for gate dielectric, tunneling barrier, and protection coating due to its excellent dielectric properties, strong adhesion to dissimilar materials, and thermal and chemical stabilities. Therefore, the Al_2O_3 layer with high bandgap can be used for preventing the thermionic emission from low bandgap TiO_2 in MOS capacitors The electrical characteristics of ALD–TiO_2/Al_2O_3 on $(NH_4)_2S$ treated InP were investigated in this study.

2. Experimental setup

Zn doped p-type InP(100) with the carrier concentration of 5×10^{17} cm^{-3} was used as the substrate. InP cleaned with only acetone is used as a reference to check the role of the native oxides. For $(NH_4)_2S$

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treated samples, the InP substrate was degreased in solvent and followed by chemical etching in a solution (H_2SO_4: H_2O_2: $H_2O = 5: 1: 1$) for 3 min to remove the surface damage and undesirable impurities and then rinsed in deionized water. After cleaning, the InP substrate was immediately dipped into the $(NH_4)_2S$ solution (10 ml of 21% $(NH_4)_2S$ solution mixed with 15 ml of DI water) at 50 °C for 40 min [11] and then blown dry with nitrogen gas (N_2). After the $(NH_4)_2S$ treatment, the InP substrate was ex-situ thermally treated at 220 °C for 10 min in N_2 to desorb the excess of weakly bonded sulfur for better electrical properties of MOS capacitor (MOSCAP) [11].

A horizontal cold-wall ALD system was used to grow ALD–TiO_2. Tetraisopropoxytitanium ($Ti(i\text{-}OC_3H_7)_4$) was used as Ti precursor and kept at 24 °C. N_2 was used as the carrier gas and its flow rate was 10 sccm. Nitrous oxide gas (N_2O) was used as an oxidizing agent and its flow rate was 100 sccm. The oxidation-resist molybdenum susceptor was used. The reactor pressure was kept at 665 Pa during the growth. The growth temperature and the deposition cycle were kept at 250 °C and 50. For ALD–Al_2O_3, alternating pulses of $Al(CH_3)_3$ (Al precursor) and H_2O (oxygen precursor) in N_2 carrier gas were used. The oxidation-resist stainless steel susceptor was used. The reactor pressure was kept at 13.3 Pa during the growth. The growth temperature and the deposition cycle were kept at 250 °C and 30. The physical thicknesses of TiO_2/Al_2O_3/InP are 5/2.9 nm/InP, respectively. The film thicknesses are examined by high-resolution transmission electron microscopy (HR-TEM). The deposition rates of TiO_2 and Al_2O_3 were about 1 and 0.97 Å/cycle, respectively. The model of TEM is JEOL TEM-3010 analytical scanning transmission electron microscope, and the operating voltage is 200 kV. The sample is prepared by SMI 3050 focus ion beam (FIB) system.

For the fabrication of MOS capacitor to examine the electrical characteristics, In (90%)–Zn (10%) alloy was evaporated on the back side of InP substrate as ohmic contact and thermally annealed at 400 °C for 3 min in N_2 atmosphere. Al was evaporated on dielectric films as the top contact with the area of 7.07×10^{-4} cm^2. Agilent B1500A semiconductor device analyzer and Agilent E4980A capacitance–voltage (C–V) meter were used for current–voltage (I–V) and 1 MHz C–V characterizations, respectively. The D_{it} value was derived by the high-low frequency (1 MHz-quasistatic) capacitance method. The quasistatic C–V was measured by HP 4156. The dc bias is swept at 1/20 V/s and provides a sufficiently accurate D_{it} value [19].

3. Results and discussion

Fig. 1 shows the I–V characteristics of TiO_2 (5 nm) on InP without and with $(NH_4)_2S$ treatment (identified as TiO_2/InP and TiO_2/S-InP, respectively). The current density limitation is set at 1.4 A/cm^2. For TiO_2/InP MOSCAP, the high leakage currents and the low breakdown electric field (E_{BR}) are observed in curve (a). The E_{BR} is defined as the electric field with the sudden current increase. For TiO_2/S-InP MOSCAP, the leakage currents are obviously improved to 5.2×10^{-5} and 4.7×10^{-3} A/cm^2 at ±2 MV/cm as shown in curve (b). Obviously, the $(NH_4)_2S$ treatment improves the leakage currents of several orders from the reduction of native oxides and sulfur passivation on InP and hence improves the interface and TiO_2 film qualities. With the stack of Al_2O_3, the leakage current densities of TiO_2/Al_2O_3/InP MOSCAP are much improved to 1.3×10^{-6} and 2.7×10^{-5} A/cm^2 at ±2 MV/cm as shown in curve (c). They are caused by the self-cleaning capability and thermionic emission decrease from high bandgap ALD–Al_2O_3. The leakage current densities of TiO_2/Al_2O_3/S-InP MOSCAP are further improved to 6.4×10^{-8} and 7.8×10^{-7} A/cm^2 at ±2 MV/cm as shown in curve (d). It shows that both ALD–Al_2O_3 self-cleaning and $(NH_4)_2S$ treatments can twofold improve the interface quality. The HR-TEM image of TiO_2/InP was used as a reference shown in Fig. 2(a). The rough TiO_2/InP interface is caused by the native oxides. For TiO_2/Al_2O_3/S-InP shown in Fig. 2(b), the clear Al_2O_3/S-InP interface reveals the removal of native oxides by both ALD–Al_2O_3 self-cleaning and $(NH_4)_2S$ treatments. Moreover, amorphous films can prevent the high leakage current associated with the grain boundary of polycrystalline film.

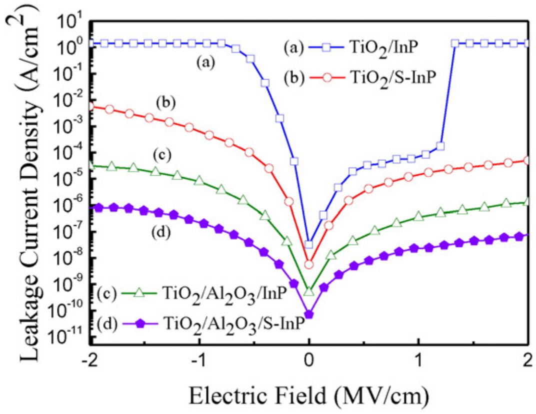

Fig. 1. I–V characteristics of (a) TiO_2/InP, (b) TiO_2/S-InP, (c) TiO_2/Al_2O_3/InP, and (d) TiO_2/Al_2O_3/S-InP MOSCAPs.

The model of AFM is SEIKO E-sweep system SPA-300 HV. The AFM measurements were performed in the noncontact mode. The microfabricated silicon cantilever with a bending spring constant of about 12 N/m and a resonance frequency of about 120 kHz were used for imaging in air with a 20 μm scanner. The scan rate is 0.5 Hz. The

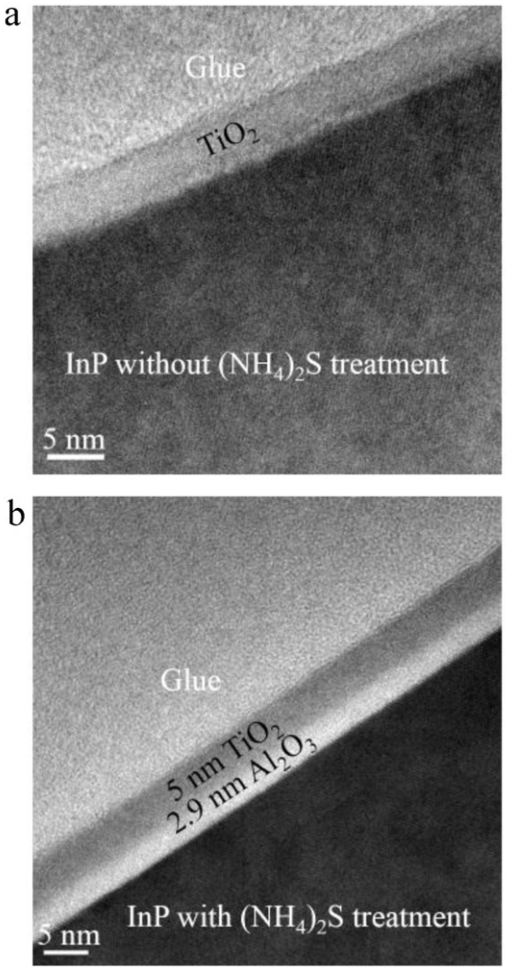

Fig. 2. HR-TEM images of (a) TiO_2/InP and (b) 5 nm TiO_2/2.9 nm Al_2O_3/S-InP structure.