Title
Al-doped HfO2/In0.53Ga0.47As metal-oxide-semiconductor capacitor

Permalink
https://escholarship.org/uc/item/20j7165d

Journal
Applied Physics Letters, 98

Author
Stemmer, Susanne

Publication Date
2011

DOI
10.1063/1.3575569

Peer reviewed
Al-doped HfO₂/In₀.₅₃Ga₀.₄₇As metal-oxide-semiconductor capacitors

Yoontae Hwang,¹ Varistha Chobpattana,¹ Jack Y. Zhang,¹ James M. LeBeau,² Roman Engel-Herbert,³ and Susanne Stemmer¹,4

¹Materials Department, University of California, Santa Barbara, California 93106-5050, USA
²Department of Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina 27695, USA
³Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania 16802, USA

(Received 24 February 2011; accepted 20 March 2011; published online 4 April 2011)

Hafnium oxide gate dielectrics doped with a one to two percent of aluminum are grown on In₀.₅₃Ga₀.₄₇As channels by codeposition of trimethylaluminum (TMA) and hafnium tertbutoxide (HTB). It is shown that the addition of TMA during growth allows for smooth, amorphous films that can be scaled to ~5 nm physical thickness. Metal-oxide-semiconductor capacitors (MOSCAPs) with this dielectric have an equivalent oxide thickness of 1 nm, show an unpinned, efficient Fermi level movement and lower interface trap densities than MOSCAPs with HfO₂ dielectrics grown by sequential TMA/HTB deposition. © 2011 American Institute of Physics. [doi:10.1063/1.3575569]

The development of metal-oxide-semiconductor field-effect transistor (MOSFET) technology with high-mobility III–V semiconductor channels faces serious challenges because of the inherently large interface trap densities (Dᵢₙ) of dielectric/III–V interfaces. For III–V n-channel MOSFETs, In₀.₅₃Ga₀.₄₇As is the leading candidate because it has a low electron effective mass, a high saturation velocity, low inter-valley scattering, and is lattice-matched to InP. Most studies of dielectric/In₀.₅₃Ga₀.₄₇As interfaces have focused on Al₂O₃, HfO₂, or ZrO₂ dielectrics. Progress has been made in reducing the Dᵢₙ of Al₂O₃/In₀.₅₃Ga₀.₄₇As and HfO₂/In₀.₅₃Ga₀.₄₇As interfaces to allow for Fermi level movement across the entire upper half of the band gap and into the lower half. In contrast, dielectric/In₀.₅₃Ga₀.₄₇As interfaces with large Dᵢₙ show limited Fermi level movement in the upper band gap and are effectively pinned near midgap for practical gate biases. Even the best interfaces, however, still exhibit significant midgap Dᵢₙ, which causes a pronounced frequency dispersion at negative gate biases in capacitance-voltage (CV) measurements. Because of the small band gap of In₀.₅₃Ga₀.₄₇As this frequency dispersion is detected even in room temperature measurements. Furthermore, scaling of these gate stacks has been extremely limited, in particular for Al₂O₃, which has a low dielectric constant (k ~ 9). Typical accumulation capacitances of well-behaved metal-oxide-semiconductor capacitors (MOSCAPs) on In₀.₅₃Ga₀.₄₇As are around 1 μF/cm², corresponding to an equivalent oxide thickness (EOT) of ~3 nm (the accumulation capacitance of MOSCAPs with In₀.₅₃Ga₀.₄₇As is lower than the oxide capacitance, Cₒₓ, because of the low density of conduction band states). Although EOTs of less than 1 nm have been reported for ZrO₂ and HfO₂ dielectrics, these have been accompanied by large Dᵢₙ and Fermi level pinning, as evidenced by a very large frequency dispersion at negative gate biases and failure to reach the depletion capacitance under negative bias. Recently, TaSiO gate dielectrics on In₀.₅₃Ga₀.₄₇As have been reported with high accumulation capacitance (1.7 μF/cm²) and low frequency dispersion. Because the dielectric constant of TaSiO (k ~ 20) is not significantly higher than that of HfO₂, and the Dᵢₙ is most likely determined by the III–V surface, rather than the specific dielectric, the goal of the study presented in this letter was to investigate if a process could be developed for hafnium-based dielectrics with both low EOT and Dᵢₙ.

Substrates were commercial, As-capped, 300 nm thick n-In₀.₅₃Ga₀.₄₇As layers (Si: 1 × 10¹⁷ cm⁻³) grown by molecular beam epitaxy (MBE) on (001) n⁺-InP (IntelliEpi, Richardson, Texas). Before gate dielectric deposition, the As cap was removed in-situ by heating and monitoring the surface using reflection high-energy electron diffraction to obtain (2 × 4)-reconstructed In₀.₅₃Ga₀.₄₇As surfaces [a mixture of β and γ-type (2 × 4)]. The dielectric was deposited in an ultrahigh vacuum MBE chamber by coevaporation of trimethylaluminum (TMA) and hafnium tertbutoxide (HTB) at a substrate temperature of 400 °C. The flux of TMA (pTMA) was varied between 20 and 180 mtorr (gas inlet baratron pressure), while the HTB flux (pHTB) was fixed at 330 mtorr. No carrier gas or additional oxygen was supplied. Samples were annealed ex situ at 400 °C for 5 min in ultrahigh purity nitrogen in a rapid thermal annealing system. 50-nm-thick Pt top electrodes were deposited by electron beam deposition through a shadow mask. A postmetal deposition anneal was carried out at 400 °C for 50 min in forming gas (95% of N₂ and 5% of H₂) to anneal out the damage in the In₀.₅₃Ga₀.₄₇As caused by the metal gate deposition, which otherwise results in a substrate punch-out. CV and conductance-based methods were used for determination of Eqs. 5.88, 5.90, and 5.91 in Ref. 11. Capacitance and conductance measurements were corrected for series resistance (Eqs. 5.88, 5.90, and 5.91 in Ref. 11). Capacitance and conductance-based methods were adapted for III–V MOSCAPs to correctly analyze the interface characteristics, as described in detail elsewhere. Calculated, ideal (no Dᵢₙ), high-frequency CV curves take the low conduction band density of states of In₀.₅₃Ga₀.₄₇As and the nonparabolicity of the I⁻ valley into account.

Figure 1 shows scanning electron microscopy (SEM) images of film surfaces grown with different TMA/HTB flux.
ratios. For small TMA/HTB flux ratios [Fig. 1(a)] the films grow in island mode similar to HfO₂ (Ref. 12) and are not fully coalesced. Even larger grains are observed for too large TMA/HTB flux ratios [Fig. 1(c)]. In the intermediate flux ratio regime [Fig. 1(b)], however, smooth, coalesced films are obtained that can be scaled to thicknesses below 5 nm without pinholes. Transmission electron microscopy (TEM) showed that the as-deposited films are amorphous. Unlike crystallized HfO₂ films, the films can be wet-etched using diluted hydrofluoric acid. X-ray photoemission spectroscopy showed that the films contained about 1.5% of Al. The role of TMA in acting as a surfactant for HfO₂ growth also benefits the growth of smooth films during the codeposition of TMA and HTB. The suppression of crystallization is typical for mixtures in which structurally complex crystalline phases require extensive atomic rearrangement and are kinetically inhibited.¹⁵

Figure 2(a) shows the CV characteristics of a MOSCAP with a ∼5 nm thick Al-doped HfO₂ dielectric that was grown under optimized conditions (p_{TMA}/p_{HTB}=0.12). The accumulation capacitance at 1 MHz is 1.85 μF/cm² at a gate voltage of 2 V, slightly higher than that for TaSiO.⁹ The inset shows the comparison with the ideal calculated CV. Filling of higher lying valleys was not included in the calculated CV, as no evidence for this (such as a step in the capacitance) was seen in the experiments. From comparison with the calculated CV, C_{st} is estimated to be 3.1 μF/cm², corresponding to an EOT of ∼1 nm, in excellent agreement with the dielectric constant estimated from a thickness series (18±3) and the physical thickness measured in TEM. The dielectric constant is similar to that reported in the literature for hafnium aluminate dielectrics with a few percent of Al.¹⁶

The depletion capacitance density is close to its ideal value (0.119 μF/cm²) for the dopant concentration of 10¹⁷ cm⁻³ (see inset), which indicates that negative biases fully deplete the channel and that the Fermi level moves past midgap. In addition, the midgap D_{it} response, apparent in the CV as a frequency-dependent “hump” at negative gate bias, is relatively small. For comparison, Fig. 2(b) shows the CV of a MOSCAP with a HfO₂ dielectric grown after short exposure of the In₀.₅₃Ga₀.₄₇As surface to TMA but without TMA added during growth.¹⁴ In this process HfO₂ could only be scaled to ∼1.4 μF/cm² accumulation capacitance density (physical film thickness: 8–9 nm) without dramatically increasing the D_{it}.¹⁴ Note the relatively larger and wider hump at negative biases, which shows that the HfO₂ MOSCAP has a larger midgap D_{it} than the MOSCAP with the dielectric grown by TMA/HTB codeposition. We note that the amount of Al in the film in Fig. 2(a) is too small to result in a detectable flat band voltage shift as may be expected due to the negative charge caused by large amounts of Al.¹⁷

Figure 3 shows a map of normalized parallel conductance, [(G_p/ω)/Aq], as a function of frequency and gate bias for the MOSCAPs with Al-doped HfO₂ and HfO₂ dielectrics shown in Fig. 2. Here, G_p is the parallel conductance, ω the angular frequency, A the MOSCAP area, and q the elemen-
MOSCAP with the dielectric grown by TMA/HTB codeposition and the dielectric grown on TMA-exposed In$_{0.53}$Ga$_{0.47}$As. The insets show the measured conductance for the MOSCAPs also differs in the accumulation region with a factor of 2.5. The improvement in Fermi level response for the hafnium aluminate MOSCAP in Fig. 3(b) is due to a combination of larger oxide capacitance and lower $D_{it}$. The latter can be estimated by multiplying $[(G_p/\omega)/Aq]_{\text{max}}$ with a factor of 2.5. The conductance of the MOSCAPs also differs in the accumulation region (positive gate bias, see insets in Fig. 3). For the MOSCAP with the dielectric grown by TMA/HTB codeposition, the conductance is decreasing with increasing positive bias. In contrast, the conductance is higher for the pure HfO$_2$ dielectric. The lower conductance for the hafnium aluminate MOSCAP can be estimated (see Ref. 8). At a gate bias of $-1.5$ V, the band bending of the In$_{0.53}$Ga$_{0.47}$As channel was more than 0.6 eV from the flat band condition and the $D_{it}$ is $6 \times 10^{12}$ eV cm$^{-2}$ near midgap (0.3 eV below the conduction band edge), which is similar to the value obtained from the conductance map.

In summary, we have shown that by codepositing small amounts of TMA, HfO$_2$ gate dielectrics can be scaled to a 1 nm EOT value, while at the same time avoiding the large midgap $D_{it}$ and effective Fermi level pinning that are commonly observed for highly-scaled HfO$_2$-based dielectrics on In$_{0.53}$Ga$_{0.47}$As. The results demonstrate that careful optimization of dielectric deposition processes, in particular obtaining a thin, dense dielectric, can lead to improvements in the electrical quality of the dielectric/III–V interface.

The research was funded by the Semiconductor Research Corporation through the Nonclassical CMOS Research Center (Task ID 1437.005). We thank Tom Mates for help with the XPS analysis. The work made use of the UCSB Nanofabrication Facility, a part of the NSF-funded NNIN network.