Achieving 1 nm capacitive effective thickness in atomic layer deposited HfO$_2$ on In$_{0.53}$Ga$_{0.47}$As

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A capacitive effective thickness (CET) value of 1.0 nm has been achieved in atomic layer deposited (ALD) high $\kappa$ dielectrics HfO$_2$ on In$_{0.53}$Ga$_{0.47}$As/InP. The key is a short air exposure under 10 min between removal of the freshly grown semiconductor epilayers and loading to the ALD reactor. This has led to minimal formation of the interfacial layer thickness, as confirmed using x-ray photoelectron spectroscopy and high-resolution transmission electron microscopy. The measured electrical characteristics of metal-oxide-semiconductor diodes of Au/Ti/HfO$_2$(4.5 nm)/In$_{0.53}$Ga$_{0.47}$As showed a low leakage current density of $3.8 \times 10^{-4}$ A/cm$^2$ at $V_{FB}+1$ V, which is about eight orders of magnitudes lower than that of SiO$_2$ with the same CET. The capacitance-voltage curves show an overall $\kappa$ value of 17–18, a nearly zero flatband shift, and an interfacial density of states $D_0$ of $2 \times 10^{12}$ cm$^{-2}$ eV$^{-1}$. © 2008 American Institute of Physics.

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Continuous downscaling of gate dielectrics has been essential to improve the performance of the complementary metal-oxide-semiconductor (CMOS) devices. The quest for technologies beyond the 22 nm node CMOS has now called for research activities on high $\kappa$ gate dielectrics on channel materials with high carrier mobility. III-V compound semiconductors of In$_x$Ga$_{1-x}$As, with $x$ varying from 0 to 1 (GaAs to InAs), are known to have electron mobility 6–18 times higher than Si. In particular, In$_{0.53}$Ga$_{0.47}$As, with its lattice matched to InP, has been used as a backbone for almost all the high-speed electronic devices; for example, high electron mobility transistors (HEMTs) with a high cutoff frequency. Shortcomings such as high gate leakage currents inevitably encountered in the HEMTs with Schottky gates, however, can be circumvented in MOS devices using insulating gate dielectrics.

Among several approaches to effectively passivate In$_x$Ga$_{1-x}$As surface, ultrahigh vacuum deposited Ga$_2$O$_3$(Gd$_2$O$_3$) (Refs. 2–5) and atomic layer deposited (ALD) Al$_2$O$_3$ (Refs. 6–10) have given a low interfacial density of states ($D_0$) and a low electrical leakage current density. The MOS diodes or MOS field-effect-transistors (MOSFETs) fabricated using these two methods have the high $\kappa$ dielectrics directly deposited on InGaAs, similar to the traditional configuration of SiO$_2$/Si. On the other hand, other efforts using deposited Si, and Ge inserted as interfacial layers between GaAs and gate dielectrics (deposited using sputtering) have also shown good electrical properties and device performance.

For further scaling of CMOS technology, HfO$_2$ with a dielectric constant (>15) much higher than that of Al$_2$O$_3$ (Refs. 7–9) is naturally more attractive as the gate oxide. ALD-HfO$_2$ was recently employed to effectively passivate In$_{0.53}$Ga$_{0.47}$As and to determine the energy-band parameters. Key for the passivation is the removal of arsenic oxides from the ALD-HfO$_2$/In$_{0.53}$Ga$_{0.47}$As interface during the ALD. However, residual native oxides of Ga$_2$O$_3$ and In$_2$O$_3$ remained at the interface. The quality of the high $\kappa$ dielectrics/substrate interface was found to be critical for affecting equivalent oxide thickness (EOT) scaling. To reduce the inevitable formation of native oxides on In$_{0.53}$Ga$_{0.47}$As/InP surface upon air exposure, in this work, we have deliberately shortened the exposure time to ~10 min, for removing freshly molecular beam epitaxy (MBE) grown In$_{0.53}$Ga$_{0.47}$As/InP from the MBE chamber and loading it to the ALD reactor for HfO$_2$ deposition. Based on high-resolution x-ray photoelectron spectroscopy (HR-XPS) and high-resolution transmission electron microscopy (HR-TEM), we found that the amount of residual native oxides at the HfO$_2$/InGaAs interface was drastically reduced, compared to the interfacial oxides observed in the HfO$_2$/InGaAs sample with longer air exposure of the In$_{0.53}$Ga$_{0.47}$As surface for at least one day prior to ALD. Moreover, the measured capacitance-voltage curves of the MOS diodes of shorter air exposure are much improved with less dispersion in the accumulated regime and with a higher $\kappa$ value about 17–18. A capacitance equivalent thickness (CET) of 0.95–1.06 nm has now been achieved in this work without any surface pretreated process.

The MBE and the ALD growth chambers are separate but in close proximity. The deposition of HfO$_2$ has been carried out in a warm-wall type ALD reactor. Liquid tetraakis-(ethyl-methyl-amine)-hafnium (TEMAH) was used as metal precursor along with H$_2$O as the oxidant source. Argon was used as precursor carrier and purged gas. One cycle time is defined as TEMAH pulse 0.5 s, Ar purge 4 s, H$_2$O pulse 0.5 s, and final Ar purge 4 s. The oxide deposition pressure was maintained at 1 torr with substrate temperatures held at 200 °C.

HR-XPS was performed at room temperature, using a SPECS-PHOIBOS-150 hemispherical electron analyzer and a dual anode x-ray source (Mg K$\alpha$ and Al K$\alpha$), to determine the chemistry at the surface and bulk of the HfO$_2$ films and at...
the oxide/semiconductor interface. The detailed XPS experimental procedure was described previously.7 Photoelectron peaks were observed and resolved by spectrum synthesis in which the spectral line shapes were simulated by the Gaussian–Lorentzian function of line shapes after subtracting a Shirley background.

The microstructure of HfO2/InGaAs was studied using HR-TEM (JEOL 2100F). MOS diodes with Au/Ti as the metal gate were fabricated by thermal vaporization and e-beam through a shadow mask. To minimize the series resistance in electrical measurements, an AuGe/Ni/Au layer was deposited on the back sides of the MOS diodes as the back contact. The current-voltage (I-V) and capacitance-voltage (C-V) characteristics of the MOS capacitors were measured using Agilent 4156C and 4284.

Since the As 2p3/2 and In 3d3/2 core levels overlap with the Hf 4p Auger peak and Hf 4p core level, respectively, only the As 2p1/2 and In 3d3/2 were used in the analysis. The XPS spectra of the As 2p1/2, Ga 2p3/2, and In 3d3/2 core levels of two HfO2/In0.53Ga0.47As samples subject to different amounts of air-exposure time of the In0.53Ga0.47As surface prior to ALD are shown in the upper panel of Fig. 1 for 13 day (long) exposure and in the lower panel of Fig. 1 for 10 min (short) exposure. The native oxides of In0.53Ga0.47As were normally 2–3 nm thick, consisting of Ga2O3, In2O3, As2O3, and a very small amount of Ga and In suboxides (as observed using HR-TEM and HR-XPS, but not shown here) after long air exposure. Surprisingly, most of them were removed after ALD growth of HfO2 with the remaining interfacial oxide thickness no more than 0.5 nm, as indicated from HR-TEM [Fig. 2(a)]. It consists of Ga2O3, In2O3, and In(OH)3 but without arsenic oxides (as shown in the upper panel of Fig. 1). The interface in the absence of elemental arsenic and arsenic oxide, as evidenced from the As 2p1/2 core level spectrum, may attribute to the unpinning of C-V characteristics. This is similar to our previous finding on ALD-Al2O3/In0.15Ga0.85As.7

Native oxides also form on In0.53Ga0.47As surface upon 10 min air exposure but are much thinner than those of long exposure, as expected. Consequently, less amounts of Ga2O3, In2O3, and In(OH)3 at the HfO2/In0.53Ga0.47As interface are revealed from the Ga 2p3/2 and In 3d3/2 core level spectra. As determined from Fig. 1, the amounts of residual native oxides of Ga2O3 and In2O3 at the interface with short air exposure are about 50% and 80% of those respective oxides for the sample with long air exposure. Moreover, In(OH)3 is negligible at the interface of the sample with short air exposure, and the residual oxides at the interface are in the order of less than two atomic layer thick. Hence it may be regarded merely as a transitional layer rather than an interfacial layer.

The cross-sectional HR-TEM studies showed an interfacial layer at most 0.5 nm thick in the sample of long air exposure [Fig. 2(a)], about two Ga–O or In–O bond lengths. However, an atomically sharp and smooth oxide/semiconductor interface with almost no interfacial layers has been observed in the sample of short air exposure [Fig. 2(b)]. The difference is consistent with the HR-XPS results. Upon forming gas annealing (375 °C 30 min), the oxide microstructure remains unchanged as amorphous with the same thickness of 4.5 nm.

Figure 3 shows the C-V curves of MOS diode for the short air-exposure sample after postoxide annealing at 375 °C 30 min in forming gas ambient. With frequency varying from 1 MHz to 10 kHz, the C-V curves show clear accumulation, depletion, and inversion. The interfacial density of states (D0) is about $2 \times 10^{12} \text{cm}^{-2} \text{eV}^{-1}$ near the mid-gap determined by the Terman method. Comparison of a theoretical C-V curve with a zero $D_0$ to the measured data at 1 MHz gave a nearly zero flatband shift ($\Delta V_{FB}$), as shown in the inset of Fig. 3. Also, the $\Delta V_{FB}$ dispersion with measured frequencies of the short-exposure sample is smaller than that of the long-exposure sample. This may be attributed to the difference in the interfacial layers for the two samples. Neve...
In summary, we have achieved a low CET of 1.0 nm, excellent C–V curves with very small flatband shift dispersion with frequencies, and low electrical leakage current densities in ALD-HfO$_2$/In$_{0.53}$Ga$_{0.47}$As/InP heterostructures without any surface pretreatments on InGaAs prior to HfO$_2$ deposition. The short air exposure plays a critical role in obtaining a clean and sharp oxide/InGaAs interface of nearly free residual oxide layer, which in turn has attributed to the excellent electrical characteristics and downsizing EOT. The scalability of low leakage, ALD HfO$_2$ to a CET of 1.0 nm on In$_{0.53}$Ga$_{0.47}$As makes it promising for future III-V MOSFET applications. Furthermore, the work is now being extended to in situ ALD growth of high k oxides directly on a freshly grown InGaAs surface by MBE. We believe that this is the ultimate solution for full understanding and precise control of the formation of the interface.

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