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Exploring metalorganic chemical vapor deposition of Si-alloyed Al_2O_3 dielectrics using disilane

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ABSTRACT

The alloying of Al_2O_3 films with Si is a promising route to improve gate dielectric properties in Si- and wide-bandgap- based MOS devices. Here we present a comprehensive investigation of alloyed film growth by metalorganic chemical vapor deposition (MOCVD) using trimethylaluminum, disilane, and oxygen precursors over a variety of temperature and flow conditions. Binary growth rates of Al_2O_3 and SiO_2 were evaluated to explain the aggregate growth kinetics of Si-alloyed Al_2O_3 films, and refractive indices were used to monitor Si incorporation efficiencies. The temperature dependence of the reaction rate of disilane with oxygen was found to be similar to that of trimethylaluminum and oxygen, leading to well-behaved deposition behavior in the kinetic and mass-transport controlled growth regimes. Compositional predictability and stability was achieved over a wider growth space with disilane-based growths as compared to previous work, which used silane as the Si precursor instead. *In situ* (Al,Si)O/n-GaN MOS gate stacks were grown and showed increasing reduction of net positive fixed charges with higher Si composition.

1. Introduction

Wide-bandgap semiconductors are emergent technologies for high-power driven applications. However, a serious hindrance to the realization of high-reliability MOS-based devices is the lack of a suitable gate dielectric [1,2]. Although Al_2O_3 is recognized as a promising candidate due to its large band offsets and high dielectric constant, the bulk and interfacial qualities are still limiting device reliability in practice. Aluminum silicate films (Al_2O_3-SiO_2) have been proposed as gate insulators in MOS devices, owing to better thermal stability compared to alumina films and their retention of amorphous structure over a larger temperature range [3]. It was suggested that the addition of Si into Al_2O_3 could compensate defects generated in the film deposition process [4]. Early reports show evidence that adding Si improved the dielectric bulk and interfacial properties in SiC, Si, and GaN MOS-structures [4–6]. The studies demonstrated suppression of gate leakage current as well as reductions to the interface-state density, flat-band shift and hysteresis. Other works have proposed that incorporating Si-O into high-κ dielectrics diminishes the scattering mechanisms associated with their highly polarizable bonds [7]. Inserting even a thin SiO_2 interfacial layer between a high-κ dielectric and Si channel could screen such scattering effects and boost electron mobility. In related experiments, the mobility in Si-MOSFET channels increased when Hf-silicate dielectrics were implemented compared with non-alloyed HfO_2 dielectrics [8]. These reported benefits from alloying dielectrics with Si evidence a compelling strategy towards improving gate dielectrics for wide-bandgap MOS devices.

Due to the novelty of developing high-κ-silicate dielectrics for wide-bandgap devices, more systematic deposition studies are needed to identify broad process windows (*e.g. via* temperature, pressure, precursors) for achieving deliberate control over the alloy composition and associated dielectric properties. The flexibility of process parameters in metalorganic chemical vapor deposition (MOCVD) can enable such opportunities, provided if the selection of precursors and their chemical compatibility are considered appropriately. Early MOCVD growth studies of Si-alloyed Al_2O_3 films were performed using various precursors such as single-source aluminum siloxide, aluminum-tri-*sec*-butoxide as the alumina source, and tetraethyl orthosilicate or hexamethyldisilazane as the silica sources [9–11]. Here, the main purpose of this work is to develop Si-alloyed Al_2O_3 gate dielectrics tailored to GaN-based applications. Developing oxide growth processes and control in a commercial technology shared with GaN-based manufacturing using standard precursors provides advantageous capabilities such as easy integration as well as *in situ* passivation of III-

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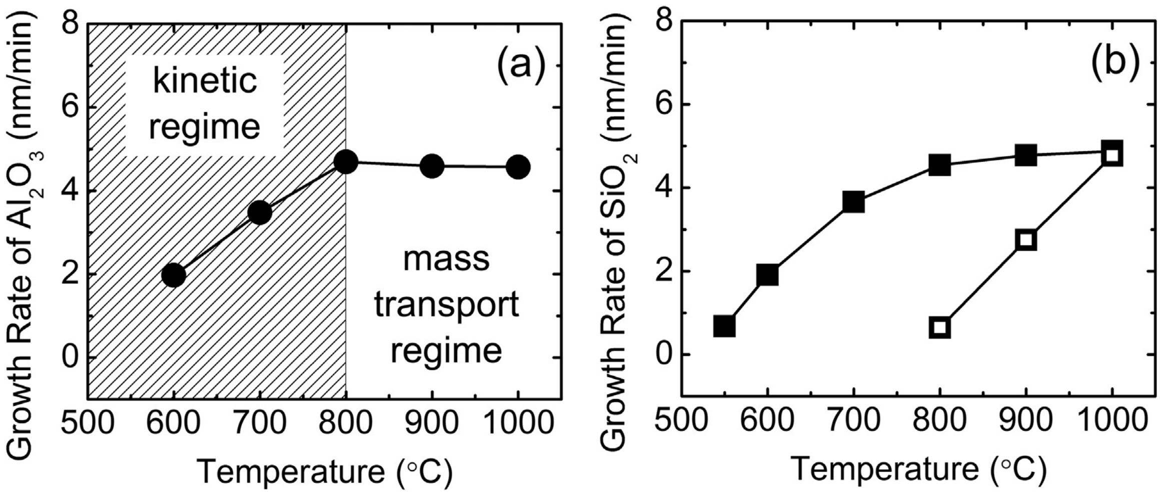

Fig. 1. Temperature dependent growth rates of (a) Al_2O_3 and (b) SiO_2 using disilane (solid square) and silane (open square) as the Si precursors.

nitride surfaces and low-defect interface formations. Accordingly, trimethylaluminum (TMA) and disilane (Si_2H_6) were selected as precursors of interest as they are compatible with and used extensively in III-nitride growth in the same reactor. Trimethylaluminum is typically employed in AlGaN growth and disilane is a common source for n-type doping of (Al)GaN. O_2 is the oxidizing agent for both TMA and disilane.

This paper studies the effects of the MOCVD growth parameters temperature, TMA and O_2 precursor flows on the Si incorporation efficiency into Al_2O_3 films as well as the impact on the kinetics governing ternary growth. The first paper on Si-alloyed Al_2O_3 films on GaN preceding this work used silane as the Si precursor. For continuity, Si-alloyed Al_2O_3 will be termed as (Al,Si)O here and in future work. A comparative analysis of the (Al,Si)O growth will be made between the two Si precursors. Finally, the impact of varying Si composition in the (Al,Si)O dielectric on its fixed charge in GaN MOS gate stacks was investigated. Though the scope of this work was developed for GaN-based devices, the application of (Al,Si)O gate dielectrics could be extended to other semiconductors as well.

2. Experimental procedure

The MOCVD reactor was a commercial Thomas Swan 1×2″ system with a closed-coupled-showerhead design. The oxidizer O_2 had 99.9999% purity and Si precursor source Si_2H_6 was 1% in N_2. N_2 was the carrier gas for all precursors, with a total flow of 10 slm that entered the chamber during growth. The reactor pressure was held at 100 Torr. For ease of measuring film thicknesses and refractive indices by ellipsometry, all (Al,Si)O films in this work were grown on 2-in. Si(001) substrates. These film properties were measured with variable angle spectroscopic ellipsometry (VASE) using a J.A. Woolam M2000DI ellipsometer over the wavelength range of 193 – 1690 nm. Thickness was determined using CompleteEASE software, assuming an oxide/(native SiO_2)/Si structure that followed the Cauchy dispersion model. Refractive index was extracted at a wavelength of 632.8 nm. The presented growth rates and refractive indices are values averaged from multiple measurements across the 2-in. wafer to accommodate for slight radial nonuniformity. Under the investigated growth conditions, the film uniformities in the thickness and refractive index were within 5% and 1% respectively of the measured average value. The fitting error in each measurement is three orders of magnitude less than the measured value, making error estimates reasonably negligible.

For the temperature-dependent growth studies of the binary oxides, the temperature was varied from 600 to 1000 °C for Al_2O_3 and from 550 to 1000 °C for SiO_2 grown by disilane. TMA and Si_2H_6 flows were 16 µmol/min and 8 µmol/min, respectively and O_2 flow was 100 sccm. Upon identifying the temperature ranges for where kinetic and mass-transport deposition processes occur, (Al,Si)O growth studies were carried out in more detail at a chosen temperature in each regime. Accordingly, (Al,Si)O growths at both 700 and 900 °C were explored. The (Al,Si)O growth rates and refractive indices were measured as a function of TMA flow (µmol/min) and O_2 flow (sccm). The investigated O_2 flow range from 50–480 sccm corresponds to 2.2–21 mmol/min. The binary oxides of Al_2O_3 and SiO_2 were also grown under the same range of precursor flows.

The Al, Si, and O compositions were determined from X-ray photoelectron spectroscopy measurements using a Kratos Axis Ultra XPS system with a monochromated Al X-ray source. Composition was extracted using the CASAXPS software. By mapping XPS-extracted composition to its measured refractive index, ternary compositions can be identified rapidly and simply *via* ellipsometry for future growth and film characterizations.

In order to assess the impact of Si concentration on oxide fixed charge properties, metal-oxide-semiconductor capacitors (MOSCAPs) were fabricated for C-V testing. The MOSCAP structures consisted of nominally 25-nm thick (Al,Si)O films of varying Si composition on the following GaN stack: 600 nm n^- (2×10^{17} cm^{-3})/800 nm n^+(2×10^{18} cm^{-3})/400 nm unintentionally doped GaN on a sapphire substrate. The oxide deposition was performed *in situ* following the growth of the GaN stack. Further details of the MOSCAP growth and fabrication process can be found in reference [12]. C-V measurements of the (Al,Si)O MOSCAPs were performed using an Agilent B1500A Parameter Analyzer. The DC bias sweep rate was 200 mV/s and the signal amplitude and frequency were 50 mV and 1 MHz, respectively.

3. Results and discussion

Fig. 1 depicts growth rates of (a) Al_2O_3 and (b) SiO_2 as a function of temperature, which features results of SiO_2 deposited using disilane with SiO_2 results replotted from our previous study [6] that employed silane instead. This comparison reveals distinct pyrolysis thresholds, where disilane cracks at a much lower temperatures compared to silane. This comparison is in agreement with findings in the literature, where disilane has been found to be more reactive at lower temperatures than silane [13,14]. Due to the higher thermal stability of silane, its pyrolysis is strongly temperature dependent over a wide temperature range, resulting in kinetically limited SiO_2 growth up to 1000 °C. On the other hand, the kinetically controlled growth regimes of SiO_2 grown using disilane and Al_2O_3 ended at around 800 °C, where the binary oxides transitioned into a mass-transport controlled growth regime. This allows for improved (Al,Si)O growth control at lower deposition temperatures.