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Research Article

Thermal Stability of Neodymium Aluminates High-κ Dielectric Deposited by Liquid Injection MOCVD Using Single-Source Heterometallic Alkoxide Precursors

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Thin films of neodymium aluminate ($NdAlO_x$) have been deposited by liquid injection metalorganic chemical vapor deposition (MOCVD) using the bimetallic alkoxide precursor $[NdAl(OPr^i)_6(Pr^iOH)]_2$. The effects of high-temperature postdeposition annealing on $NdAlO_x$ thin films are reported. The as-deposited thin films are amorphous in nature. X-ray diffraction (XRD) and medium energy ion scattering (MEIS) show, respectively, no crystallization or interdiffusion of metal ions into the substrate after annealing at 950°C. The capacitance-voltage *(C-V)* and current-voltage *(I-V)* characteristics of the thin films exhibited good electrical integrity following annealing. The dielectric permittivity (κ) of the annealed $NdAlO_x$ was 12, and a density of interface states at flatband (D_{it}) of 4.01×10^{11} cm^{-2} eV^{-1} was measured. The deposited $NdAlO_x$ thin films are shown to be able to endure high-temperature stress and capable of maintaining excellent dielectric properties.

1. Introduction

Recently, considerable effort has been exerted in developing high-κ rare earth oxide, M_2O_3 (M = La, Pr, Nd, etc.), as a replacement of the conventional SiO_2-based gate dielectric material [1]. The incorporation of neodymium (Nd) ions in insulating layers has important applications for solid-state laser materials, luminescent materials, protective coatings, and gate dielectric applications [2, 3]. However, Nd_2O_3 is thermally unstable upon annealing and can be partially transformed to NdO(OH) when exposed to atmospheric conditions [4]. One of many solutions to enhance the thermal stability is the incorporation of aluminium (Al) to develop innovative multifunctional advanced lanthanide-aluminates-based ceramics, $MAlO_3$ (M = La, Pr, Gd, and Nd). The lanthanide aluminates are promising high-κ candidates as they combine the advantages of the high permittivity of the lanthanide oxide with the chemical and thermal stability of Al_2O_3. Furthermore, they remain amorphous up to high temperatures, leading to a large reduction in leakage current relative to polycrystalline M_2O_3 films during CMOS processing [5, 6].

Work on $NdAlO_x$ was mostly reported as a ceramic material for microwave applications and as a diffusion barrier in solid-oxide fuel cells [7, 8]. Growth of $NdAlO_x$ thin films have previously been achieved by various deposition methods, including pulsed laser deposition [9], chemical vapor deposition [10, 11], e-beam evaporation [8], and atomic layer deposition [4]. To date, however, little is still known about the physical and electronic characteristics of $NdAlO_x$ due to a lack of suitable precursors with appropriate stability, volatility, and decomposition characteristics. This has motivated us to further exploit these perovskite thin films

for gate dielectric applications using an alternative single-source precursor. The use of single-source precursor allows better mixing of the components at atomic level, significantly lower decomposition temperature, and free from halide ions contamination [11].

In this work, the effects of high-temperature postdeposition annealing (PDA) on the properties of the $NdAlO_x$ thin films, deposited by metalorganic chemical vapor deposition (MOCVD) using single-source precursor, were studied.

2. Experimental

Near stoichiometric $NdAlO_x$ thin films (Nd/Al = 0.87) were deposited on n-type silicon (100) substrates by liquid injection MOCVD at 450°C on an Aixtron AIX 200FE AVD reactor fitted with the "TriJet"™ liquid injector system [12], utilizing the single-source precursor $[NdAl(OPr^i)_6(Pr^iOH)]_2$. Selected films were subjected to high-temperature (750–950°C) postdeposition annealing (PDA) in pure nitrogen (N_2) ambient for 60 seconds. Subsequently, a postmetallization forming gas anneal (FGA) was carried out at 400°C for 30 minutes using $H_2 : N_2$ in the ratio 1 : 9, together with a control as-deposited sample.

X-ray diffraction (XRD) was performed on the studied films using nickel-filtered Cu Kα radiation (λ = 1.5405 Å) with a 2θ increment of 0.2° per second. The samples were scanned over a $\theta/2\theta$ range of 20° to 40°. Medium energy ion scattering (MEIS) experiments were carried out using a nominal 200 keV He^+ ion beam and a 70.5° scattering angle. Cross-section transmission electron microscopy (TEM) was carried out using a JEOL 2000 FX operated at 500 kV. Capacitance-voltage (*C-V*) measurements were conducted on the MOS capacitors of the structure (Au/$NdAlO_x$/SiO_2/n-Si) using a HP4192 impedance analyzer, with 30 mV RMS probe signal, at various frequencies (1 kHz–1 MHz). Leakage current (*I-V*) measurements were obtained using a Keithley K230 programmable voltage source and a 617 type electrometer.

3. Results and Discussion

Phase transitions of the gate dielectric, as a function of PDA temperatures, were accessed by X-ray diffraction (XRD). The X-ray diffraction traces of the as-deposited and PDA samples (regardless of PDA temperature) exhibited a diffraction peak consistent with the (200) peak from the silicon substrate. No other diffraction features were observed (Figure 1(a)), suggesting that they were essentially amorphous. In addition, MEIS results indicated that no significant level of crystallinity or movement of metal ions was in evidence in the 950°C PDA film as demonstrated in Figure 1(b).

Figure 2 shows TEM micrographs in which the thicknesses of the high-κ stack, including the interfacial layer, were evaluated. The high-κ thickness and a thin native oxide interlayer, adjacent to the silicon substrate, changed from 11 nm and 1.5 nm, respectively, and to 10.4 nm and 2.5 nm respectively, after 950°C PDA. This could be due to interdiffusion of oxygen between SiO_2 and $NdAlO_x$. The growth

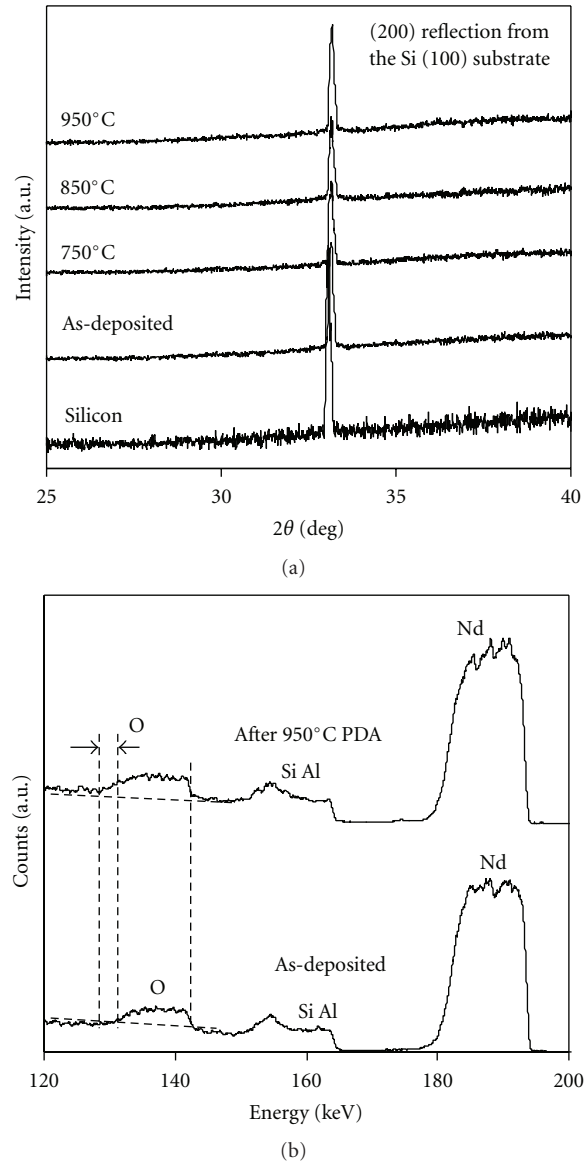

Figure 1: (a) X-ray diffraction traces for $NdAlO_x/SiO_2$ stacks as a function of RTA temperatures. (b) A comparison of MEIS data of a $NdAlO_x/SiO_2$ stack prior to and after RTA in pure N_2 ambient for 1 min.

of the SiO_2 layer, following annealing, is also visible in the MEIS energy spectrum (Figure 1(b)). The amorphous nature of the thin films is also observed in the TEM analysis (Figure 2) confirming the XRD findings.

The high-frequency *C-V* characteristics of as-deposited and PDA samples are shown in Figure 3. Both as-deposited and PDA samples *exhibited* small counter-clockwise hysteresis (<0.1 V). A positive shift of flatband voltage (V_{FB}) (the shift of V_{FB} is 0.97 V) in the as-deposited sample was observed and contributed to fixed negative oxide charges. However, a near-ideal flatband voltage (V_{FB} = 0.65 V) was obtained in the 950°C PDA sample. This may indicate that negative fixed oxide charges could be compensated by nitrogen-induced positive fixed oxide charges generated

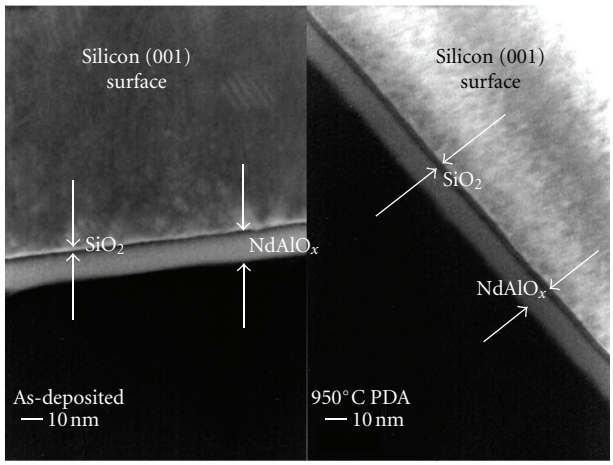

FIGURE 2: TEM image of the as-deposited and 950°C PDA $NdAlO_x/SiO_2$ stacks shows the thicknesses of oxide layers change from 1.5 nm/11 nm to 2.5 nm/10.4 nm, respectively.

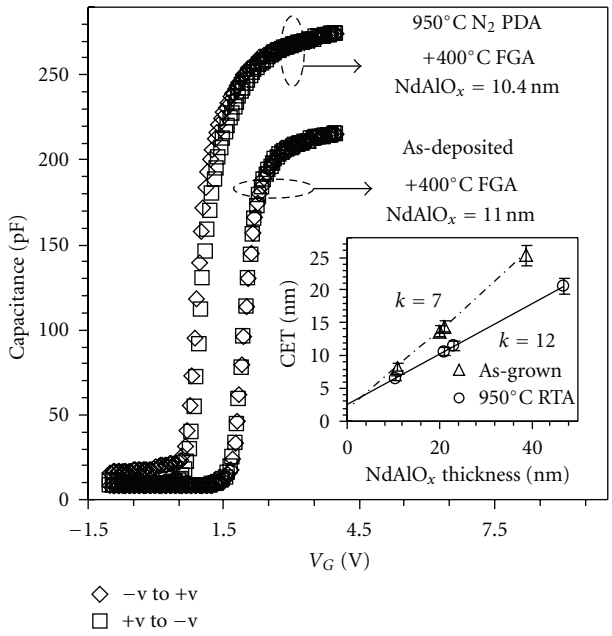

FIGURE 3: A comparison of high-frequency *C-V* curves with and without N_2 PDA treatment. MOSCs with [Au/$NdAlO_x$/SiO_2/n-Si/Al] structure were fabricated with an effective area of 4.9×10^{-4} cm^{-2}. The inset is a plot of capacitance equivalent thickness (CET) versus $NdAlO_x$ physical thickness, which shows an increase in the dielectric permittivity (7 to 12) and changes of the interfacial layer (1.5 to 2.5 nm) after PDA treatment.

during annealing at the $NdAlO_x/SiO_2$ interface. Terman analysis [13] yields an interface density of states, D_{it}, of 4.94×10^{11} cm^{-2} eV^{-1} and 4.01×10^{11} cm^{-2} eV^{-1} at midgap for as-deposited and 950°C PDA samples, respectively. This is lower than D_{it} of other recent high-κ candidates, D_{it} of 2.5×10^{12} cm^{-2} eV^{-1} found in $La_{1.3}Hf_{1.0}O_{4.1}$ [14], but higher than the interface state density of 5×10^{10} cm^{-2} eV^{-1} shown by $Y_xHf_{1-x}O_y$ ($x = 0.065$) [15].

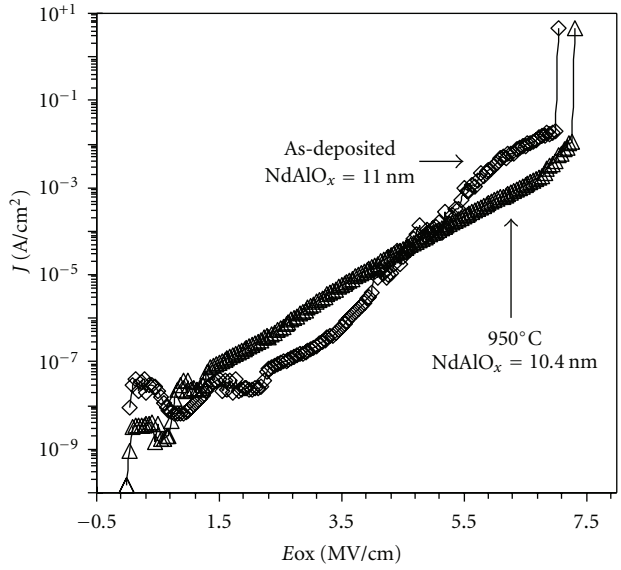

FIGURE 4: Leakage current density (J) versus electric field (Eox) applied across the $NdAlO_x/SiO_2$ stacks as a function of PDA temperatures. The $NdAlO_x$ films thickness was $t_{high-\kappa} \sim 10.4$ to 11 nm.

Despite an increase of the interfacial layer in the PDA samples, the measured capacitance in strong accumulation was found to be higher than that of the as-deposited samples. The inset of Figure 3 shows a plot of the high-κ dielectric thickness against capacitance equivalent thickness (CET). The slope revealed the $NdAlO_x$ dielectric permittivity (κ) to be 7 and 12 in the as-deposited and 950°C PDA films, respectively. The increase of dielectric permittivity (κ), observed after receiving thermal treatment, could be due to a small change of the crystal symmetry, with the formation of some small nanometer scale crystallites with higher permittivity phases of $NdAlO_x$ [16, 17].

The leakage current densities (J) at 2 MV cm^{-1} in all samples, even after 950°C PDA, were below 1×10^{-7} A cm^{-2} (Figure 4), which is comparable with other leading edge high-κ dielectrics [18]. The average breakdown, regardless the annealing treatment, also occurs at the equivalent field strength of 7 MV cm^{-1}.

4. Conclusions

The $NdAlO_x$ thin films deposited by liquid injection MOCVD have been shown to remain amorphous up to 950°C as shown by XRD analysis. No significant level of crystallinity or movements of metal ions was also in evidence after annealing at 950°C as indicated in MEIS energy spectra. Electrical properties of $NdAlO_x$ samples, after high-temperature annealing, were presented. Good electrical integrity was maintained even after 950°C PDA as shown by *C-V*and *I-V* results, showing the extracted dielectric permittivity of 12, a low leakage density of 7×10^{-7} A cm^{-2} at 2 MV cm^{-1}, and a density of interface states at flatband D_{it} of 4.01×10^{11} cm^{-2} eV^{-1}. These features

make the neodymium aluminate a potential candidate for the dielectric replacement.

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