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Metal–insulator–metal capacitors with MOCVD grown Ce–Al–O as a dielectric

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ABSTRACT

Ce–Al–O thin films were prepared on 70 nm TiN/Si(1 0 0) substrates by pulsed injection metal organic chemical vapor deposition (PI-MOCVD) for metal–insulator–metal (MIM) applications. Depositions were carried out at 400 °C using two separate Ce and Al precursors. In order to get Ce–Al–O films with different stoichiometry, Al_2O_3 and CeO_2 were mixed with different Ce:Al precursors' ratios. According to the XRD analysis, the as deposited films were amorphous if more aluminum was injected than cerium, and crystalline – if they are cerium rich. Electrical properties have been investigated in MIM capacitors after e-beam evaporation of Au top electrodes. Oxides possess a dielectric constant of 10–20 in combination with leakage current densities as low as 10^{-5} A/cm^2 at −2 V. The post deposition annealing (PDA) at 600 °C and 850 °C in N_2 for 5 min lead to the diffusion of Ti from TiN bottom electrode and formation of the rutile TiO_2 phase. Nevertheless, $CeAlO_3$ films were obtained if the ratio of injected Ce:Al was 1:1. The *k* values increased to 60 in this case, but the leakage current density worsened to 10^{-3} A/cm^2 at −2 V.

1. Introduction

The rapid increase of wireless communications products has also energized the further development of MIM capacitors, which are one of the most essential passive elements in radio frequency and analog/mixed signal integrated circuits [1]. Since the main objective is to achieve higher capacitance density per unit area, the replacement of now used SiO_2 [2,3] or Si_3N_4 [4,5] with the new alternative dielectrics, which have higher *k* value, is quite a promising approach. Due to the large bulk permittivity value (∼3000) [6], $CeAlO_3$ is an attractive dielectric material to investigate in form of thin films. In this work, we evaluate the possibility to grow thin films of Ce–Al–O for the first time by MOCVD and to investigate the properties for the use as insulators in MIM structures.

2. Experimental

Dielectric Ce–Al–O thin films with a typical thickness of 30–40 nm were deposited at 400 °C by pulsed liquid injection MOCVD technique using separate Ce and Al precursors. Precursors were delivered into the vaporizer by a simultaneous injection of solution micro-doses using two electromagnetic injectors. Ar was used as carrier gas for vapor transportation to the hot substrate where vapor decomposes and the growth of the layer occurs. O_2 was added as oxidant. The process pressure was kept at 1 mbar. All depositions were carried out on Si(1 0 0), covered with 70 nm TiN bottom electrode grown by Physical Vapor Deposition (PVD). The thickness of Ce–Al–O films was measured by means of ellipsometry. The crystallinity of the layers was studied by X-ray diffraction (XRD). Scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) were employed to study the structure and the stoichiometry of the layers. Finally, for determination of electrical properties of metal–insulator–metal (MIM) structures, Au top electrodes (400 μm) were deposited at room temperature through a shadow mask. The capacitance–voltage (*C*–*V*) characteristics were measured at 100 kHz.

3. Results and discussion

The fabrication of MIM capacitors usually requires low thermal budget; therefore at the first step, separate CeO_2 and Al_2O_3 oxides were grown at moderate temperatures. The deposition conditions had to be evaluated for these precursors, since no single source precursors, which contain both metals, exist.

The typical growth rate dependence on the deposition temperature is given in Fig. 1. As can be seen, both CeO_2 and Al_2O_3 can be grown at the temperatures as low as 250 °C. In addition, two growth regions can be clearly observed for both oxides. In the

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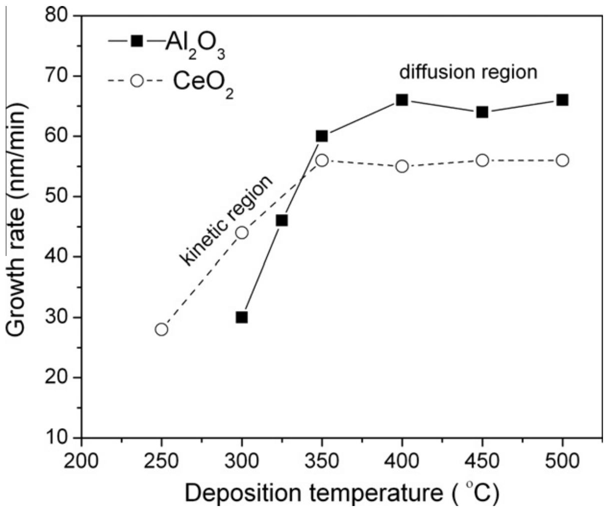

Fig. 1. Growth rate of Al_2O_3 and CeO_2 films as a function of the deposition temperature.

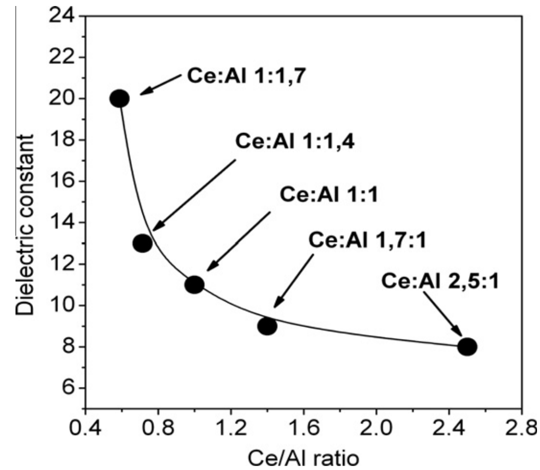

Fig. 3. Dielectric constants of as deposited Ce–Al–O MIM capacitors as a function of injected Ce:Al ratio.

vtemperature range of 250–350 °C for CeO_2 and the temperature range of 300–350 °C for Al_2O_3, the kinetic growth regimes dominates. At higher temperatures (>350 °C), the growth rate becomes nearly independent of the deposition temperature for both oxides.

For the further depositions, the process temperature of 400 °C was selected and both oxides were mixed with different Ce:Al precursors' ratios in order to get Ce–Al–O films with different stoichiometry. According to the XRD analysis, the films are crystalline if they are cerium rich (line (3) in Fig. 2), whereas the layers are amorphous (line (1) in Fig. 2) if more aluminum than cerium precursor is injected. In the case of 1:1, a small and broad CeO_2 (1 1 1) reflection is detected. The other two reflections (1 1 1) and (2 0 0) in the XRD plot correspond to the cubic orientation of PVD grown TiN.

The electrical properties of the as deposited Ce–Al–O films were extracted after performing *C–V* and *I–V* measurements in the range from −3 to +3 V. As dielectric constant can be directly extracted from the *C–V* measurements, its dependence as a function of injected Ce:Al ratio is plotted in Fig. 3. A dielectric constant of 20 is obtained if more Al is introduced into the samples. This *k* value is around a factor of two higher than the one reported for thin films of $Ce_{0.7}Al_{1.3}O_3$ prepared by MDB [7], but is far from the values of $CeAlO_3$ crystals [6]. A drop of the *k* value to 8 is observed if more Ce is injected into the films. For comparison, single Al_2O_3 has a *k* value of 9 [8], while CeO_2 possesses a dielectric permittivity of ~20 [7,9].

Another important characteristic for MIM capacitors is the leakage current density, especially at higher voltages. Its dependence on the injected Ce:Al ratio is shown in Fig. 4. As can be seen, leakage current values of $\sim 10^{-5}$ A/cm^2 can be extracted at −2 V. In addition, there is a small effect on the leakage current densities as the function of Al content in the films. The samples, which possess higher Al than Ce content, have around one order of magnitude lower leakage current densities. This effect could be attributed difference of the band gaps of the Al_2O_3 (8.7 eV) [8] compared to the one of CeO_2 (3.2 eV) [10].

Generally, high *k* values for ternary oxides are obtained for crystalline phases, but it is well known that crystallization of these compounds require higher temperatures. Therefore, in the second part of this work, the effect of post deposition annealing (PDA) on the structural and electrical properties will be presented. PDA was performed at 600 °C and 850 °C in pure N_2 for 5 min. The main goal was to obtain crystalline $CeAlO_3$ phase, which should posses a high value of the dielectric constant. The XRD data of annealed

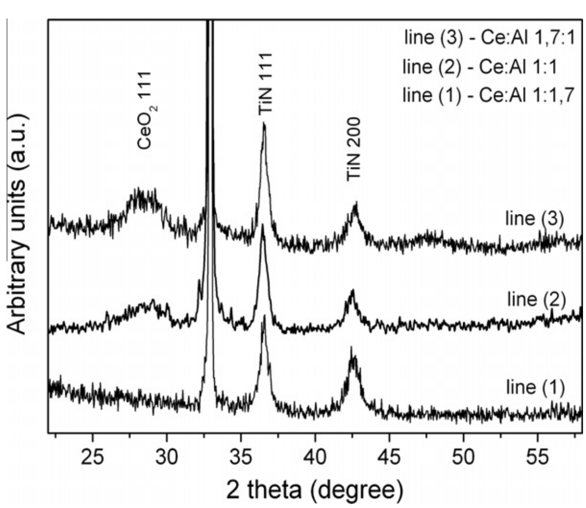

Fig. 2. XRD patterns of Ce–Al–O thin films grown with different injected Ce:Al ratios.

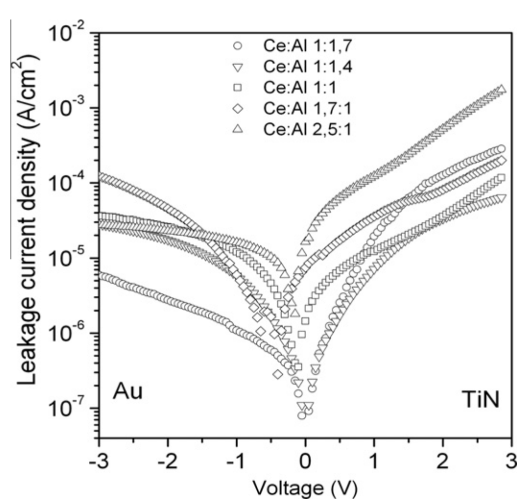

Fig. 4. Leakage current densities of Ce–Al–O based MIM capacitors prepared with different Ce:Al injection ratios.