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Tailoring the dielectric properties of $\text{HfO}_2\text{--Ta}_2\text{O}_5$ nanolaminates

Kaupo Kukli,^{a)} Jarkko Ihanus, Mikko Ritala, and Markku Leskela
Department of Chemistry, University of Helsinki, FIN-00014 Helsinki, Finland

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Dielectric thin films applicable, for instance, as insulating layers in electroluminescent display devices have been studied. In order to improve dielectric characteristics $\text{HfO}_2\text{--Ta}_2\text{O}_5$ nanolaminates were prepared by atomic layer epitaxy at 325 °C. The nanolaminates were evaluated in capacitance and current–voltage measurements. By optimizing the layer thicknesses in the nanolaminate structures the dielectric properties, especially leakage current densities, could be tailored remarkably. The best nanolaminates showed charge storage factors improved up to 8 times when compared with those of the single oxide films. The presence of nanosize crystallites of monoclinic and metastable tetragonal HfO_2 was observed by x-ray diffraction analysis. © 1996 American Institute of Physics. [S0003-6951(96)03526-7]

The search for high permittivity and low leakage dielectric thin films is actual for the development of many micro- and optoelectronic devices.^{1,2} In this study dielectric films have been examined from the point of view of thin-film electroluminescent (TFEL) displays.^{3,4} High dielectric constant, breakdown resistance, mechanical stability, and chemical inertness are the intrinsic properties required from the insulators in contact with phosphor layers.⁴ Furthermore, the already as-deposited insulators in an unannealed state must be of a high quality due to glass substrates. Here, we describe a remarkable improvement of Ta_2O_5 based high permittivity dielectrics by preparing $\text{Ta}_2\text{O}_5\text{--HfO}_2$ nanolaminates. In memory capacitors, only very thin layers could be used in such layer structures,⁵ but in TFEL devices the insulators are thicker, typically a few hundred nanometers, thereby allowing a broader variation of the individual layer thicknesses in the nanolaminates.^{4,6,7}

Owing to its unique self-limiting growth process the atomic layer epitaxy (ALE) technique^{8,9} is capable of meeting the challenge to deposit films with accurately controlled layer thicknesses uniformly over large area substrates. Pure Ta_2O_5 and HfO_2 films and their nanolaminates were grown onto patterned indium-tin-oxide (ITO) electrodes on $5 \times 5 \text{ cm}^2$ glass substrates using a hot-wall flow-type F120 ALE reactor, operated under a 10 mbar nitrogen pressure.⁸ $\text{Ta}(\text{OC}_2\text{H}_5)_5$ and HfCl_4 were evaporated from open boats held at 105 and 140 °C, respectively, inside the reactor. Water vapor was exploited as an oxygen precursor. The films were grown at 325 °C, which is the highest temperature for self-controlled growth regime for Ta_2O_5 .¹⁰

Figure 1 depicts schematically the structure of the $\text{HfO}_2\text{--Ta}_2\text{O}_5$ nanolaminates. The thicknesses of the Ta_2O_5 interlayers were varied in a range of 1.2–18.8 nm. The thicknesses of the HfO_2 layers were varied in a way that the total thickness of one $\text{HfO}_2\text{--Ta}_2\text{O}_5$ bilayer remained constant. Three main sample series with different bilayer thicknesses of 20, 10, and 5 nm were prepared. The total thickness of all multilayers was kept at about 170 nm. This was independently checked by fitting transmittance spectra measured

within a wavelength range of 370–1100 nm.¹¹ In most samples both under and top layers were Ta_2O_5 . For comparative measurements some $\text{HfO}_2\text{--Ta}_2\text{O}_5$ nanolaminates where both under and top layers consisted of HfO_2 were prepared as well. Aluminum electrodes were evaporated onto the as-deposited nanolaminates. The area of a single electrode was 29.4 mm². Capacitances were measured at 10 kHz frequency using an HP 4275A multifrequency LCR meter. The current–voltage characteristics were analyzed with an HP 4140 B pA meter/dc voltage source, or HP 4142B modular dc source. All measurements were made at room temperature. Film crystallinity was examined with x-ray diffraction (XRD) using a Philips MPD 1880 diffractometer with $\text{Cu } K_\alpha$ radiation.

To compare the properties of the different insulators for given capacitor structure, charge-storage factors (Q) as figures of merit were evaluated:¹²

$$Q = U_{cr} \cdot C/S,$$

where C is the capacitance measured, S is the electrode area, and U_{cr} is the critical voltage inducing a certain, arbitrarily chosen value of leakage current density ($1 \mu\text{A}/\text{cm}^2$). The charge-storage factor provides information about the charge stored per surface area at a given leakage current density level.

The permittivities of the pure Ta_2O_5 and HfO_2 films were 25 and 16, respectively. Due to the relatively high leak-

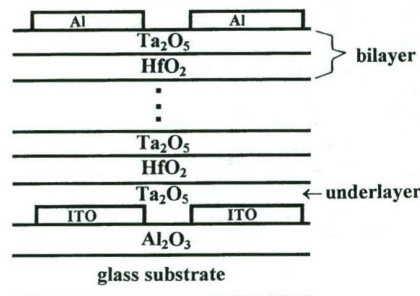


FIG. 1. Schematic representation of the nanolaminates prepared onto $5 \times 5 \text{ cm}^2$ glass substrates. The Al_2O_3 layer serves as an ion barrier against sodium diffusion from soda lime glass.

^{a)}Permanent address: Institute of Material Science, University of Tartu, EE2400 Tartu, Estonia.

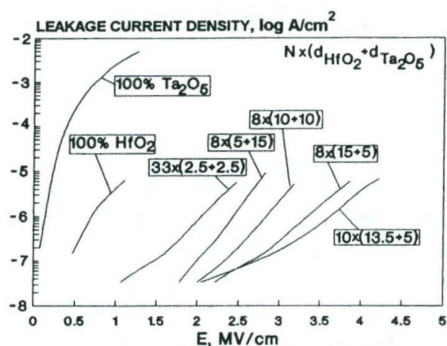


FIG. 2. Dependence of leakage current density on applied electric field strength in single Ta₂O₅ and HfO₂ films and HfO₂-Ta₂O₅ nanolaminates. Labels describe the sample configuration $N(d_{\text{HfO}_2} + d_{\text{Ta}_2\text{O}_5})$ where N is the number of bilayers, d_{HfO_2} and $d_{\text{Ta}_2\text{O}_5}$ are thicknesses of single HfO₂ and Ta₂O₅ layers, respectively, expressed in nanometers.

age currents (Fig. 2) the charge-storage factor Q was as low as 8 nC/mm² in both cases. XRD measurements indicated remarkable crystallization in the HfO₂ films (Fig. 3) while the Ta₂O₅ films were amorphous.

By preparing HfO₂-Ta₂O₅ nanolaminates the leakage currents were dramatically reduced (Fig. 2). By varying the layer thicknesses within the multilayer structure the leakage current properties could be tailored markedly (Fig. 2). The leakage current for the configuration 33(2.5+2.5) is rather similar to that measured by Kattelus *et al.*⁵ in their multilayers of 32(3+3) configuration grown by ALE from TaCl₅, HfCl₄, and H₂O at 300 °C. However, a further reduction in the leakage current density was achieved when the layer thicknesses were increased up to 15 nm (Fig. 2). An additional increment of the HfO₂ interlayer thickness above 15 nm was followed by an apparent increase in breakdown probability.

The permittivity of the multilayers decreased with increasing HfO₂ content (Fig. 4). The charge storage factor exhibited a rather broad maximum between 50% and 75% relative HfO₂ content (Fig. 5). Q values up to 66 nC/mm² were achieved in these films. Reduction of the bilayer thickness and/or the increase of the HfO₂ interlayer thickness generally led to a decrease of the permittivity (Fig. 4) and in-

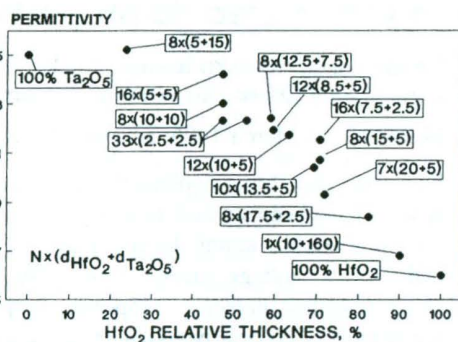


FIG. 4. Permittivities of HfO₂-Ta₂O₅ nanolaminates vs the relative thicknesses of HfO₂ layers. For labeling, see Fig. 2. For 33(2.5+2.5) configuration the results from the samples with HfO₂ lower and top layer are both indicated.

creased dielectric instability as compared with other samples having the same relative HfO₂ contents.

Polycrystalline ceramic films may exhibit increased conductivity along the grain boundaries.^{2,13,14} In the nanolaminates the intermediate amorphous Ta₂O₅ layers inhibit the continuous crystal growth of HfO₂ and, thereby, eliminate the grain boundary channels extending from one electrode to the other. The leakage current reduction in the nanolaminates can also be due to electron trapping at the interface states at the end of leakage channels extending through single sublayers, thereby causing a decrease of the injecting electric field in the vicinity of these channels.²

If the above two effects were the only mechanisms for the successful reduction of leakage currents, no differences should be observable between different configurations, provided that the films are thick enough to form continuous well-defined interlayers with their characteristic dielectric properties. In practice it was observed that the dielectric properties, also including the leakage current density, can be optimized further by varying the thicknesses of the single layers constituting the nanolaminate film. To rationalize these observations the structural properties of the nanolaminates were examined with XRD (Fig. 3).

The crystalline ITO electrode layer was found to have a strong effect on the crystallization of the HfO₂ films depos-

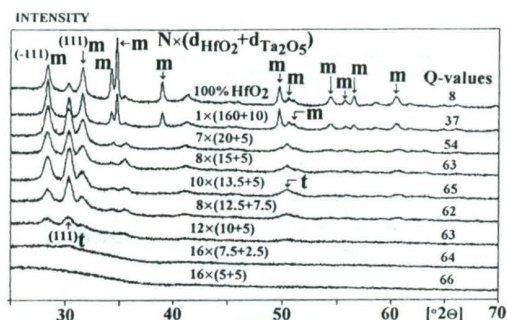


FIG. 3. XRD patterns of HfO₂ thin films and HfO₂-Ta₂O₅ nanolaminates. The labels m and t refer to the monoclinic and tetragonal HfO₂ (Ref. 15). The intensity scale is linear.

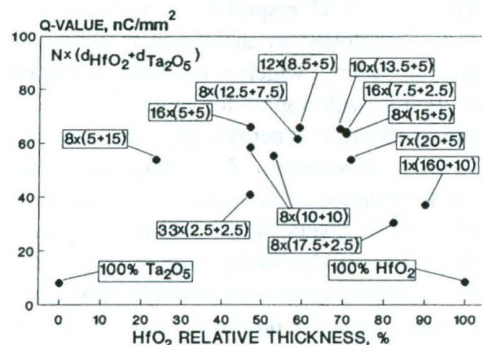


FIG. 5. Charge storage factors of HfO₂-Ta₂O₅ nanolaminates vs the relative thicknesses of HfO₂ layers. For labeling, see Fig. 2. For 8(10+10) configuration the results from the samples with HfO₂ lower and top layer are both indicated.

ited upon it. However, the effect of ITO was already eliminated after a deposition of 10 nm amorphous Ta₂O₅ between the ITO and HfO₂ films; the XRD patterns of these films were identical to those deposited on glass covered by an identical Ta₂O₅ underlayer. The XRD patterns shown in Fig. 3 were measured from samples deposited on glass.

The XRD pattern of the pure HfO₂ film (Fig. 3) is dominated by reflections of the monoclinic HfO₂ (*m*-HfO₂) phase.¹⁵ In addition, the tetragonal (111) reflection is observed as well.¹⁵ The tetragonal HfO₂ (*t*-HfO₂) is known to be a metastable phase at room temperature¹⁶ but it may be stabilized by film stress and/or grain size effects.^{16,17}

In the HfO₂-Ta₂O₅ nanolaminates crystallization of the HfO₂ is observed when the HfO₂ layer thicknesses exceed 10 nm (Fig. 3). With increasing HfO₂ layer thickness the XRD reflections become more intense and the peak widths decrease. The crystallite sizes calculated from the XRD peak widths for the *t*-HfO₂ increase from 7.5 to 14.5 nm when the thicknesses of the HfO₂ layers increase from 7.5 to 20 nm. The crystallite sizes of the *m*-HfO₂ are in a range of 9.0–11.8 nm in samples having 10–20 nm HfO₂ layer thicknesses.

The third effect of increasing layer thickness is a decrease of the relative fraction of the *t*-HfO₂ (Fig. 3). Nevertheless, in the thicker films the relative content of the *t*-HfO₂ is increased when a 10 nm thick Ta₂O₅ layer is deposited between glass and HfO₂. Thus it is suggested that the Ta₂O₅ underlayer enhances nucleation and growth of the *t*-HfO₂.

Correlation of the XRD data with the dielectric properties indicates that the nanolaminates with optimized characteristics contain a remarkable amount of *t*-HfO₂. Apparently, to attain the optimum dielectric properties the thicknesses of the HfO₂ layers should be high enough for crystallization and, on the other hand, low enough to prevent the formation of larger crystallites and leaky grain boundaries acting as weak points, and/or to keep the relative fraction of the *t*-HfO₂ high.

No differences in electrical properties were observed in the samples with otherwise similar configurations but with different under and topmost layers (Figs. 4 and 5). This enables to choose the oxide layer in TFEL structures in accord with interface properties and structural compatibility with phosphor material. For instance, Ta₂O₅ is known to have a positive effect on the structural and luminescent properties of the subsequently deposited phosphor layer,⁷ while HfO₂ generates a larger density of deep interface states.⁶

In conclusion, it has been shown that by preparing HfO₂-Ta₂O₅ nanolaminates, the lowest leakage currents

measured were about 3×10^{-8} A/cm² at 2 MV/cm which is a remarkably low value for unannealed samples. It seems that the tailoring of dielectric properties is related to the crystallization of HfO₂, though the exact mechanism cannot yet be unambiguously identified. The highest storage factors for the HfO₂-Ta₂O₅ nanolaminates exceeded that of single oxide films by about 8 times.

Thus, in the nanolaminates where high storage factors are needed, a high permittivity material with high breakdown resistivity such as Ta₂O₅ is to be used. In order to suppress the leakage currents, interlayers of low leakage current density material, e.g., HfO₂, have to be added. In such multilayer structures the amorphous Ta₂O₅ layers interrupt the grain boundaries acting as leaky channels through the polycrystalline films. While preparing nanolaminates ALE is an advantageous technique since it allows an accurate film thickness control and uniformity over large areas.

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