HfO$_2$ films grown by ALD using TDMAH and water or ammonia water

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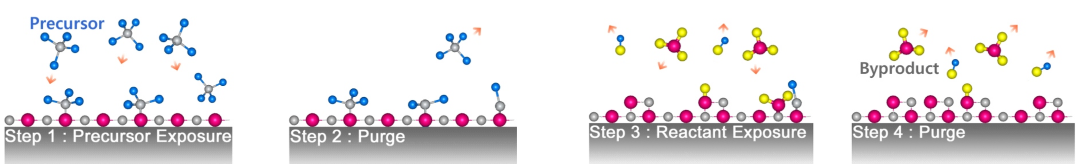
Introduction

Hafnium dioxide (HfO$_2$) is known for its many required properties and important technological applications. This significant material exhibits the following unique features, particularly, a high-k dielectric constant (~20), high permittivity, relatively large band gap (~6 eV), a high index of refraction (~1.91), good thermodynamic and chemical stability, low density of the interface state, low leakage current, excellent surface passivation performance, a wide range of UV-IR transparency area, high laser damage threshold and hardness and thermal stability. Due to the fast progress of optical applications such as plasma screens, emitters of light-emitting diodes, lasers of solid states, and many different scintillators, there is a demand for luminescent materials that are efficient and durable. These applications are often based on wide-gap materials, such as HfO$_2$ thin films, with a significant thickness of 200–700 nm and are often activated with rare earth ions. Also needs to be mentioned that the use of the HfO$_2$ insulator indicates promising results for a sensitivity of a modern dielectric modulated FET biosensor for the detection of coronavirus in terms of spike, envelope, and DNA proteins of the virus. This may be of great importance in a wide range of applications in medicine. In the production of the electronic industry, there is a demand for higher equipment performance. These demands push the progress of technology forward, which requires a thorough understanding of materials' chemical, mechanical, and physical properties, such as those found in HfO$_2$ used in typical electronic devices, especially recently based on ultra-wide bandgap semiconductors (e.g. Ga$_2$O$_3$, ZnGa$_2$O$_4$, ZnMgO, etc).

Growth method - Atomic Layer Deposition



Savannah-100 reactor from Ultratech/CNT (Veeco, San Jose, CA, USA)

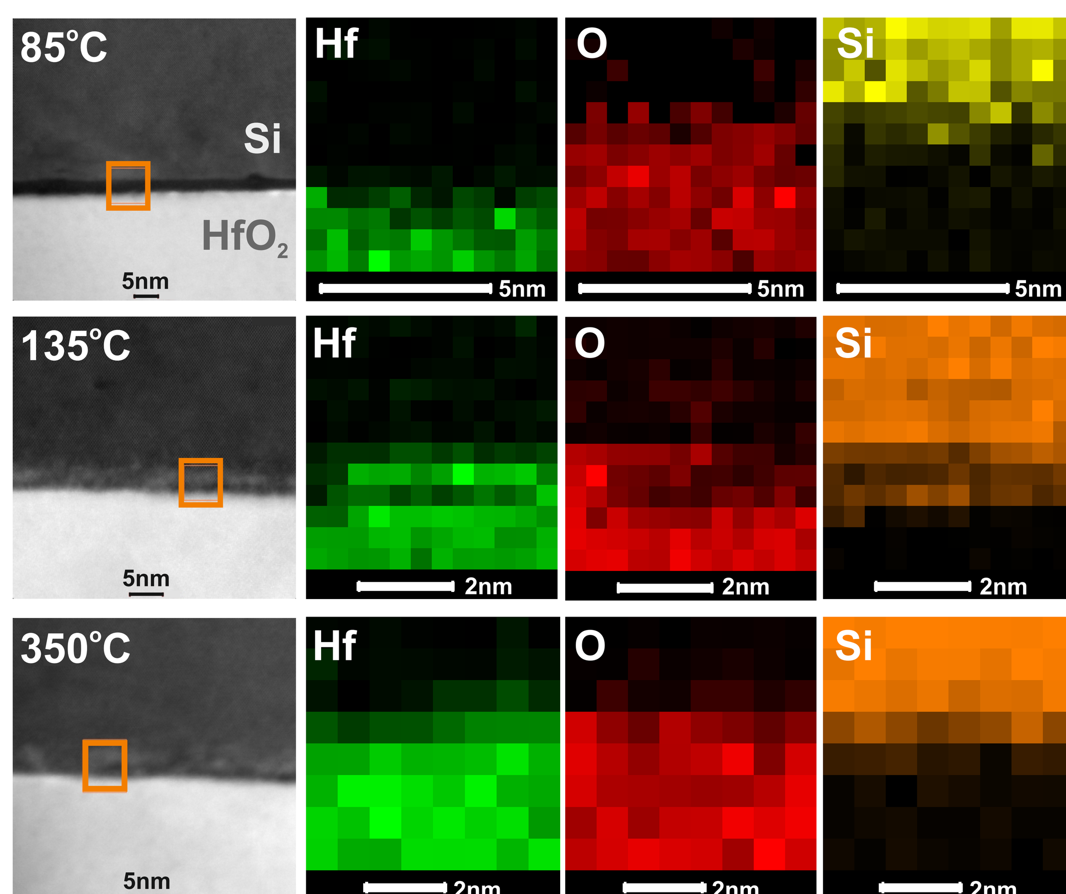
ALTERNATE SUPPLY OF COMPONENTS
- No reaction in gas phase
- Possibility of use of aggressive precursors
- Low growth temperature is possible!

HIGH UNIFORMITY
- Covering a very complicated structures

SELF-LIMMITING PROCESS
- Growth rate is NOT dependent on flux homogeneity
- Maximal growth rate 1ML per cycle

Precursors: **Hf** - Hf[(CH$_3$)$_2$N]$_4$ **N** - NH$_3$·H$_2$O **O** - H$_2$O

EDX &TEM measurements



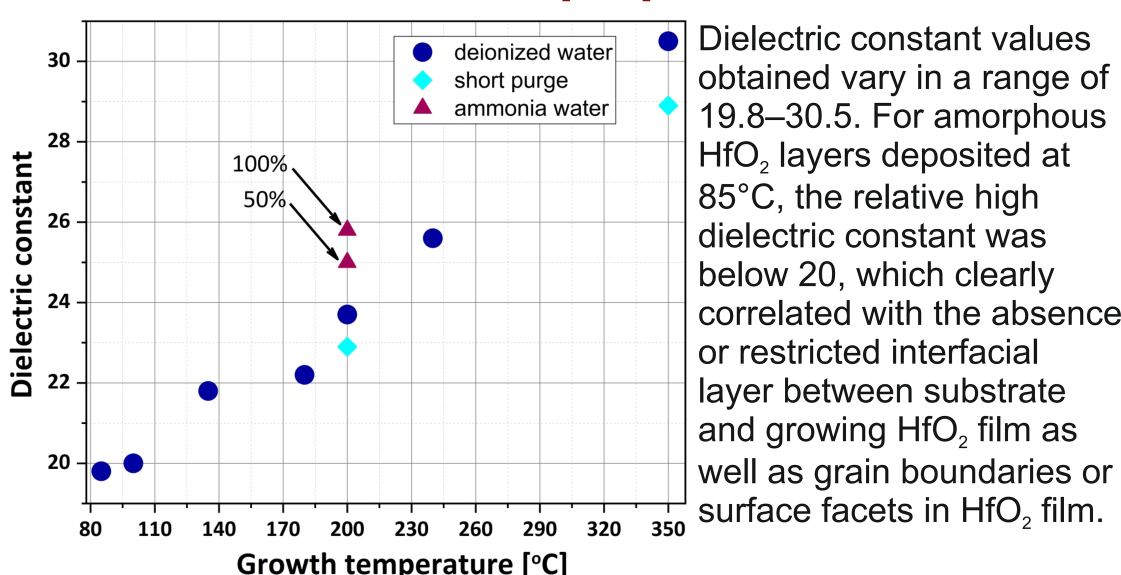
85°C 50nm Si HfO$_2$

135°C 20nm

350°C 20nm

TEM images (left) and element distribution maps of the orange square areas obtained by EDX of Hf (green color), O (red color) and Si (orange color) of HfO$_2$ films with thickness of about 100 nm. Layers were grown at substrate temperatures of (a) 85, (b) 135 and (c) 350°C on Si substrates.

Dielectric properties



Dielectric constant values obtained vary in a range of 19.8–30.5. For amorphous HfO$_2$ layers deposited at 85°C, the relative high dielectric constant was below 20, which clearly correlated with the absence or restricted interfacial layer between substrate and growing HfO$_2$ film as well as grain boundaries or surface facets in HfO$_2$ film.

Acknowledgement

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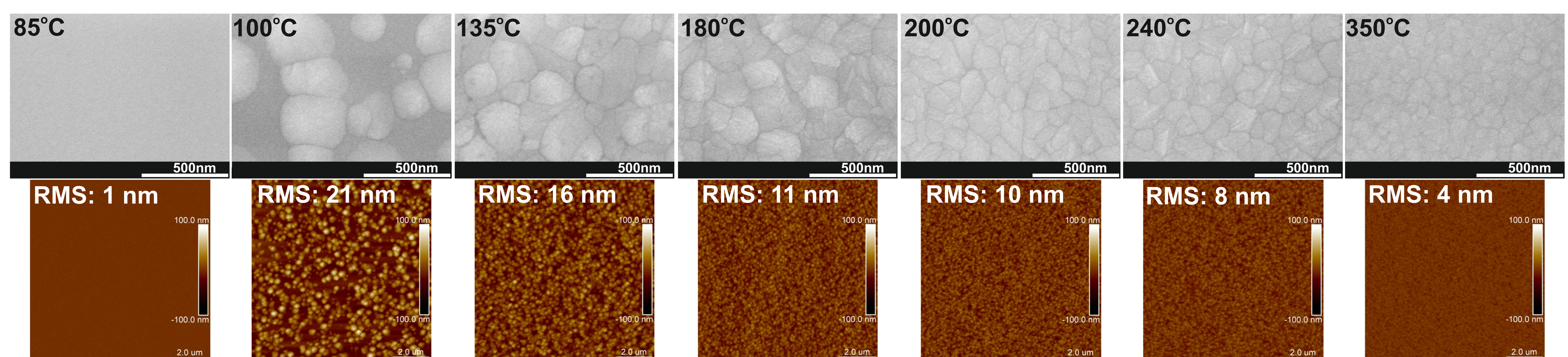
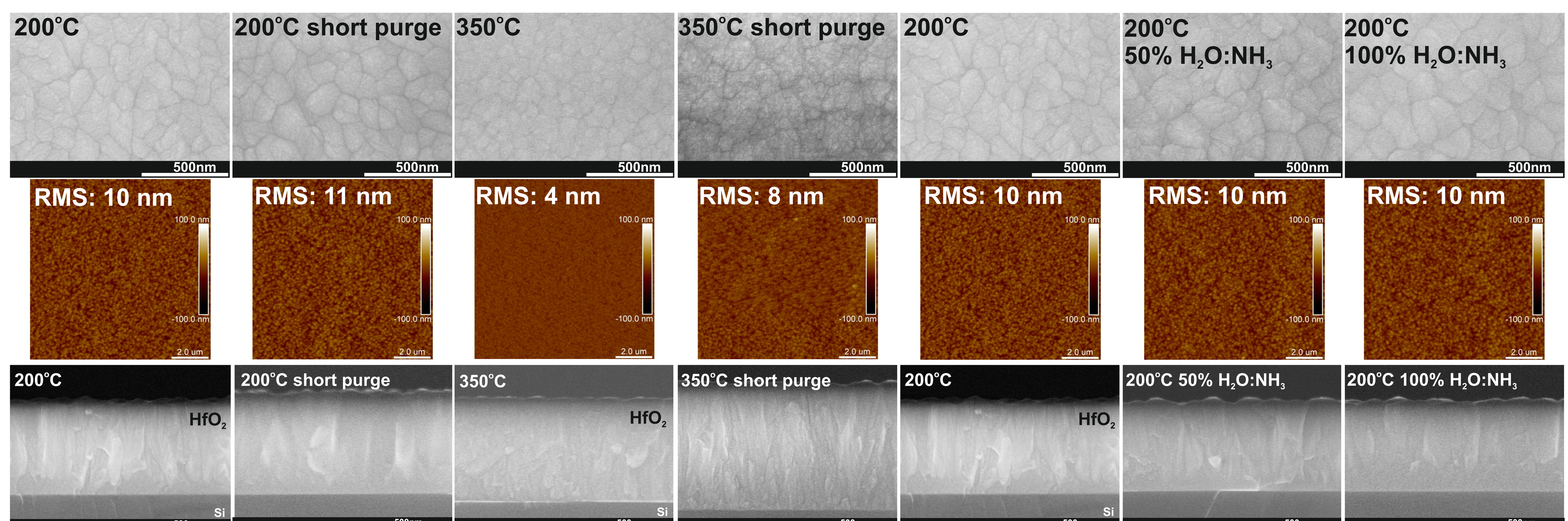
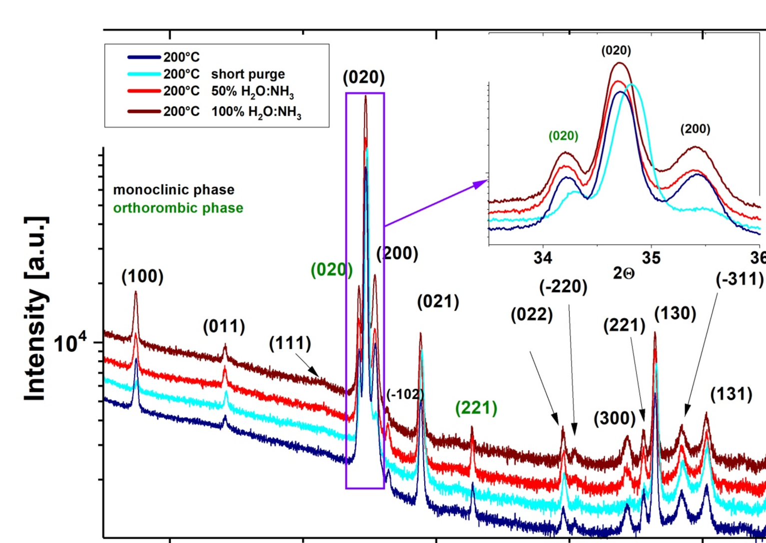
AFM &SEM measurements

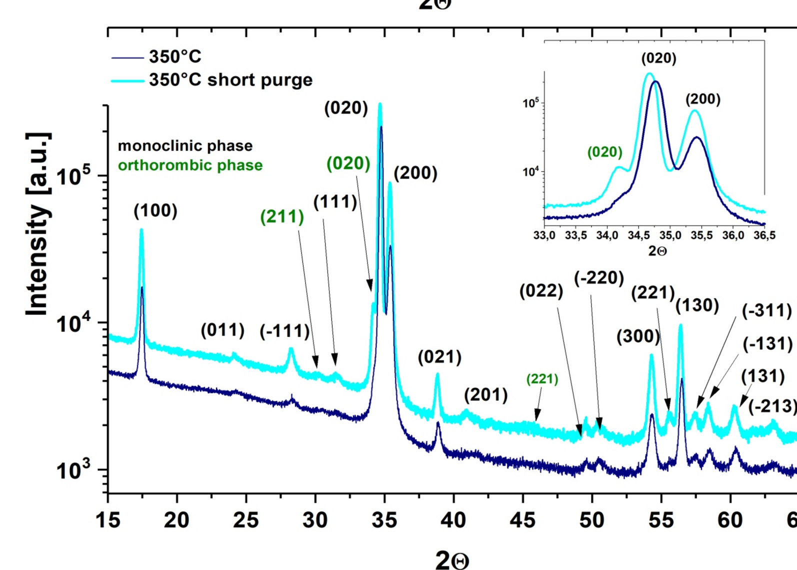


The low-temperature ALD (below 100°C) caused the formation of amorphous HfO$_2$ films with very small particles on the surface (2 nm) and a flat surface (RMS = 1 nm). When the growth temperatures were higher in the 100–350°C range, the HfO$_2$ layers had been transformed into the polycrystalline states with more oriented structure. In general, as the deposited temperature rose from 100 to 350°C, the particle sizes on the surface and RMS surface roughness decreased from 83 to 17 nm and from 21 to 4 nm, respectively. Furthermore, the use of short nitrogen purge times had significant influence on the dominant orientation of the monoclinic phase because it led to decreasing reflection intensity and the presence of peaks from monoclinic and orthorhombic phases in the XRD pattern p. This was due to the fact that the use of short purge times reduced structural order and determined a more randomly oriented polycrystalline structure in HfO$_2$ films which corresponded to the change in grain sizes, the increase in RMS surface roughness and particle sizes on surface. As already noted, these changes were most probably due to the reactions in the ALD processes that were not thoroughly completed within short nitrogen purge times.

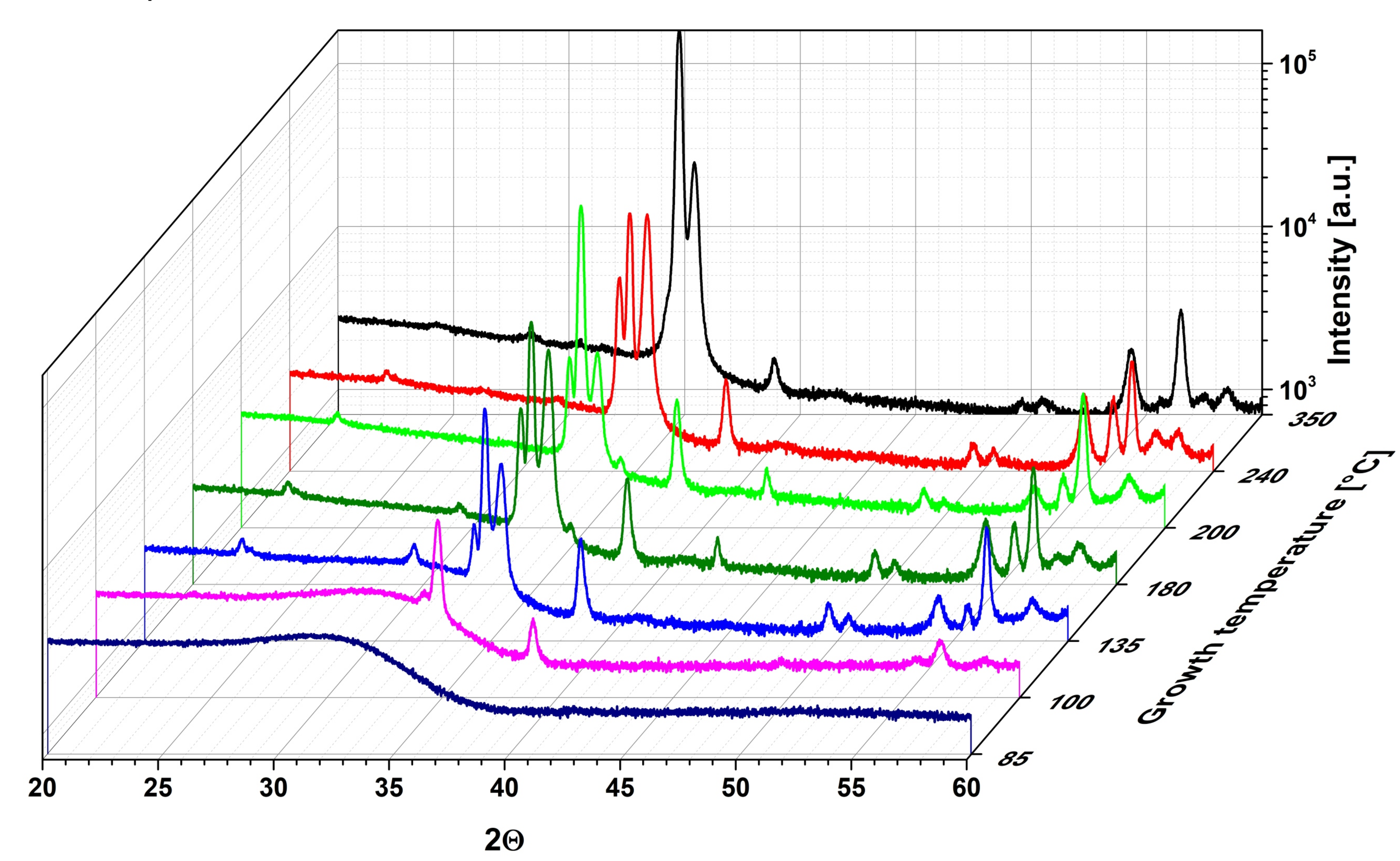


XRD measurements





XRD and TEM characterizations revealed that the HfO$_2$ films deposited at temperatures less than 100°C were amorphous, while films grown at temperatures higher than or equal to 100°C were polycrystalline. The preferred orientation of crystal growth was various in different temperatures



Conclusions

The HfO$_2$ films were found to contain different crystalline structures. Layers grown at deposition temperatures less than 100°C are amorphous, while thicker layers fabricated at higher temperatures or equal to 100°C are oriented polycrystalline films with one or two crystalline phases. Substantial reduction of surface roughening occurred along with increasing growth temperature for crystalline layers grown above 300°C, but also for amorphous layers grown below 100°C. The improvement in crystallinity in turn increased the dipole density, which is responsible for the increased relative permittivity (the dielectric constant value). These films were more densely packed. The change of the structure of the HfO$_2$ films obviously affects the electrical properties of layers, which is due to that the phase affects the strain and surface roughness of films as well as the dielectric constant.