Crystallization of HfO2 thin films and their influence on laser induced damage

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Abstract. We present our investigation on the crystallization of IBS HfO2 on (0001) SiO2. The crystallization was studied by in-situ XRD. The activation energy was 2.6±0.5 eV. The growth follows a two-dimensional mode. LIDT measurements (5000-on-1) with 10 ns pulses at 355 nm on 3QWT HfO_2 layers shows that the crystallization leads to increase of the laser irradiation resistance. The 0%-LIDT of the as coated sample was 3.1 J/cm2 and increased to 3.7 J/cm2 after 5h @ 500°C.

1 Introduction

Thin-film interference coatings, like antireflection or high reflectance coatings as well as wavelength and polarization selective coatings, are key elements of optical components as they allow to tune or even radically alter their optical properties [1,2]. Current high-end optical coatings in the VIS/NIR range are mainly based on ion beam sputtered (IBS) multilayers. Thermal annealing of a single layer or multilayer stacks is a well-established way to improve the properties like optical losses or laser irradiation resistance [3]. Above a temperature T_{cryst} the films starts to crystallize which can be wanted or unwanted. Thus, the understanding of the crystallization process, the dependence on time and temperature and the activation energy are essential for defined controlling the thermal treatment and tuning the properties.
In the case of laser applications, HfO_2 is standard high index material. Investigations show that high temperature annealing leads to the crystallization and the laser-induced damage behaviour improves [4]. In this work, investigate the crystallization of thin HfO_2 films by means of in-situ x-ray diffractometry and its effect on the laser-induced damage threshold.

2 Experimental setup and results

2.1. Crystallization

For the investigation of the crystallization, we deposited thin HfO_2-single layers with thickness of 10, 15, 20 and, 50 nm. The coating was done by means of reactive ion beam sputtering from a metallic Hf-target (Plasmaterials with 3N purity) using a Veeco Spector 1.5 Dual Ion Beam Sputter (DIBS) tool placed in a clean-room environment (ISO 5-7). In order to achieve complete oxidization the process O_2 flux during deposition was 31 sccm. The temperature during film growth was 100°C. As substrates, we used epi-polished 10x10 mm^2 SiO_2 single crystals with 0001 orientation from CrysTec. Prior coating, the samples were in-situ treated with energetic O_2 ions (1 keV) for 10 minutes using the second plasma source of the Veeco DIBS machine.
The in-situ XRD thermal annealing experiments were carried out using a Bruker D8 Discovery DaVinci diffractometer equipped with an Anton Paar DHS1100 high temperature stage. Since polycrystalline films were expected we selected a grazing incidence geometry, with $\omega = 2°$ as incoming angle. The 2θ range was 28 - 35°, which contained the expected main peaks of both the cubic and monoclinic HfO_2 [5]. Isochronal annealing on 10 nm thick HfO_2-samples in steps of 50°C and a holding time of 30 min was carried out to gain an overall view of the transformation. Based on this information, we performed isothermal scans on the 15, 20, and 50 nm thick samples with temperatures between 550 and 650°C. The period between each single scan was 6 minutes. Figure 1 shows the results of the isothermal scans of the 50 nm thick sample at a temperature of 550°C. The fitted integral value of the peaks in Fig. 1a gives the crystalline fraction for each scan, which is depicted in Fig. 1b as a function of time. As can be seen in the small inset in a logarithmic scale the measurement points can be clearly described by a linear fit function. From this the crystallization times t_c and dimensionality of the growth n' were calculated [6]. The calculated n' was between 1.85 and 2.15 for the different thicknesses and temperatures indicating 2D-growth. The corresponding Arrhenius-plots of crystallization times gives an activation energy for crystallization of 2.6±0.5 eV.

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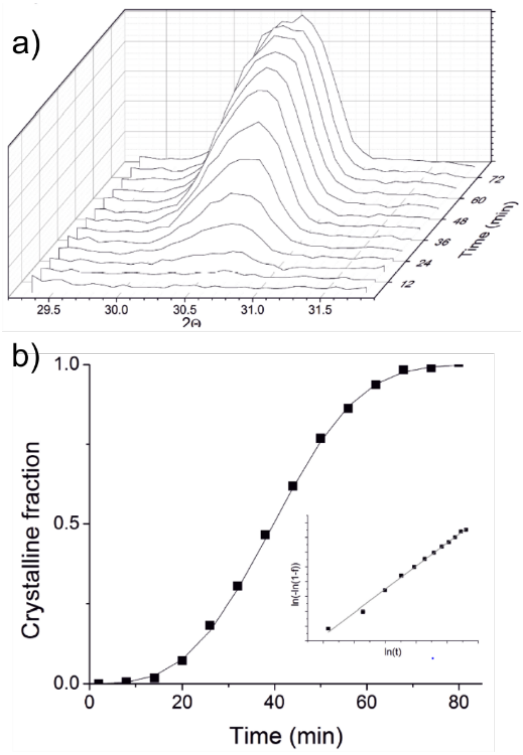

Fig. 1. Time evolution of the cubic HfO_2 111 peak of the 50 nm thick layer during the 550°C annealing a) as well as the relating fitted peak integral as a function of annealing time b). The inset shows the curve in logarithmic scale.

2.2 Laser damage testing

Applying the same coating procedure, we deposited 127 nm (3QWT @ 355 nm) thick HfO_2-single layers for the investigation of the LIDT. Therefore we used fused silica samples (P4-polished, rms roughness of about 3 Å, scratch-dig 20-10) provided by WZW Optics AG. Prior to the deposition, the samples were precision cleaned using a wet bench placed in the cleanroom. The detailed cleaning process is described in Ref. [7]. After deposition, the samples were annealed at 500°C for 1 h and 5 h, respectively. Temperature and time were chosen regarding the results of the Arrhenius-plots. Laser-damage testing was performed at 355 nm using the LIDT setup at RhySearch [7]. Pulse duration was 10 ns and the spot size (1/e) at the surface was 230 µm.
Fig. 2 shows the damage onsets as well as the 0%-LIDT values after 100 and after 5000 pulses for the different samples. The damage onset and the 0%-LIDT in case of the as-deposited (x-ray amorphous) layer are about 3.0 and 4.1 J/cm^2, respectively. The partially crystallized sample after 1h @ 500°C shows a decreased fluence for the onset and the 0%-LIDT. In contrast, the full-crystallized sample that was thermally treated for 5h @ 500°C shows a slightly higher damage onset and 0%-LIDT compared to the as-deposited sample.

3 Conclusions

Controlled nucleation and crystallization is a key for the defined and controlled improvement of optical properties of thin films like laser damage resistance. Therefore, the knowledge of growth mode, nucleation time as well as activation energy is essential. In our investigation on crystallization of HfO_2 thin films we found that an activation energy of 2.6±0.5 eV.
In accordance with the investigations of other groups [3.4] the full crystallized layer shows higher laser-induced damage resistance compared to the amorphous sample. In contrast, it seems that the intermedia state of the partially crystallized film has a significantly lower damage resistance compared to the amorphous one.
The crystallization behaviour, as well as the dependence on the optical properties, as well as the laser-induced damage resistance, will be investigate in depth in the next years.

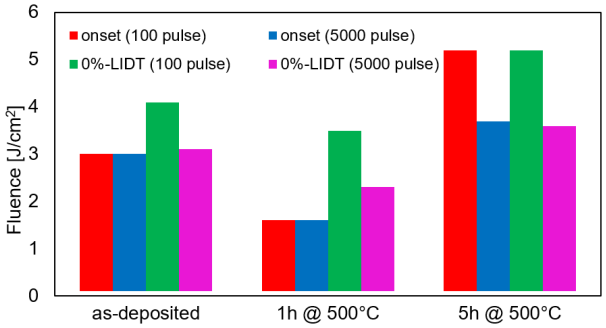

Fig. 2. Damage onsets as well as the 0%-LIDT values after 100 and after 5000 pulses for the different samples.

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