Supporting Information

The hydrogen induced fcc-fct transition in hafnium thin films

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Experimental

Thin films

The thin film samples are produced with magnetron sputtering and are composed of a 4 nm Ti adhesion layer, a 60 nm Hf layer and a 10 nm Pd capping layer. Direct current (DC) magnetron sputtering of the metallic layers is performed in 0.3 Pa of Argon and inside an ultrahigh vacuum chamber (AJA Int.) with a base pressure of $10^{-10}$ Pa. The layers were deposited on $10 \times 10$ mm$^2$ quartz substrates (thickness of 0.5 mm and surface roughness < 0.4 nm) which were rotated to enhance the homogeneity of the deposited layers. Typical deposition rates include 0.22 nm s$^{-1}$ (50 W DC) for Pd, $X$ nm s$^{-1}$ (X W DC) for Hf, and 0.05 nm s$^{-1}$ (100 W DC) for Ti. These sputter rates were determined by first sputtering each target independently at a fixed power over a well-defined time interval. Subsequently, X-ray reflectometry (XRR) was used to estimate the layer thickness of this reference sample (see below for experimental details), from which the sputter rate was computed.

Optical transmission measurements are performed using hydrogenography$^1$ using an Imaging Source 1/2.5" Aptina CMOS 2592 × 1944 pixel monochrome camera equipped with an Edmunds Optics 55-906 lens, i.e. the same camera as used in ref.$^2$ Five Philips MR16 MASTER LEDs (10/50 W) with a color temperature of 4,000 K are used as a light source and provide a white spectrum (Fig. S1). The transmission is averaged over an area of $180 \times 180$ pixels, corresponding to about 80 mm$^2$. A reference sample is used to compensate for fluctuations of the LED white light source and the contribution of the 10 nm Pd capping layer. The partial hydrogen pressures are obtained by using 0.1% and 3.5% H$_2$ in Ar gas mixtures. During the experiments a minimum gas flow of 20 s.c.c.m. is always maintained.

X-ray diffraction (XRD) and XRR measurements were performed using a Bruker D8 Discover equipped with a Cu X-ray tube (Cu-κα, $\lambda = 0.154$ nm) and a LYNXEYE XE detector. The XRR measurements were performed with a Göbel mirror and a 0.1 mm fixed slit on the primary and two 0.1 mm slits on the secondary side with the detector operated
in 0D mode. The data were fitted with GenX3 to obtain estimates for the layer thickness, roughness and density of the thin films. All data have been fitted with a three-layer model: one for the Ti adhesion layer, one for the Hf layer, and one for the Pd cap layer.

The *in situ* out-of-plane XRD measurements were performed simultaneous with the XRR measurements and thus using the same set-up as for the XRR measurements: using a Gobel mirror and a 0.1 mm slit on the primary side and two 0.1 mm slits on the secondary in combination with the detector operated in 0D mode. Differently the *in situ* in-plane XRD measurements were performed using programmable slits on both the primary and secondary side with a constant sample footprint of 6 mm. During these measurements, the detector was operated in 1D mode. All XRD measurements were fitted with a (sum of) pseudo-Voigt function(s) to extract the d-spacing.

The *in situ* XRD and XRR measurements were performed inside an Anton Paar XKR900 Reactor chamber with a base pressure of $P < 5 \times 10^{-4}$ mbar [Figure S2(a)] connected to an Anton Paar TCU 70 control unit. A solenoid inlet valve (MKS inst. 0248AC-10000SV) and a manometer (MKS inst. Baratron type 627DMCC1B) are connected to the inlet of the reactor chamber, both connected to a pressure control unit (MKS inst. type 250 controller). The outlet of the reactor chamber is connected to a mass flow controller (Brooks Instruments 150 s.c.c.m.) and subsequently a vacuum pump (Adixen Drytel 1025). An additional solenoid outlet valve (MKS inst. 0248AC-10000SV, connected to a Delta Elektronics ES030 - 5 Power Supply) is positioned parallel to the flow controller to ensure sufficient flow at low absolute pressures inside the reactor chamber. The pressure control unit, outlet valve and flow controller are controlled by a home-written National Instruments Labview code.

During the *in situ* experiments, a mixture of 0.096% H$_2$ in helium (2% relative tolerance) was used as a gas and a constant flow of at least 10 s.c.c.m. was maintained at all times. After setting the pressure we waited at least 15 min before commencing the measurement to be sure that the sample fully responded to the new pressure set point.

Several additions were made to the reactor chamber to facilitate the *in situ* in-plane XRD
measurements. First, sample holders were constructed that allow the samples to be oriented under different tilting angles $\chi$ inside the reactor chamber [Figure S2(c)]. These sample holders can be mounted on the sample position of the reactor chamber and are either made from aluminum ($\chi = 35, 70^\circ$) or 3D printed (Specifics) ($\chi = 55^\circ$). As these sample holders increase the height of the top of the sample with respect to the beam, and the window in which the sample height can be adjusted is limited to $-3.0 < z < 3.0$ mm, a 6.0 mm thick adapter plate was mounted between the sample insert of the reactor chamber and the main body of the chamber [Figure S2(b)]. As such, this allows the samples to be positioned in the center of the goniometer of the diffractometer.

**Powder**

Sponge Hf with a purity of 99.8 mass% was obtained from Mitsuwa Chemical Co., Ltd. A stainless steel tube was filled by the sample of approximately 4 g and the tube was evacuated for 1 h at 150 °C. Subsequently, the sample was deuterated under a deuterium pressure of 2 MPa at $T = 300$ °C. Deuterium gas of 4N purity was used. Afterwards, the tube was evacuated by a turbo molecular pump for 3 h at 650 °C to dedeuterate the sample. Pressure-composition isotherms at 300 °C were measured using the volumetric method (Fig. S3). Then, three deuteride samples HfD$_x$ with deuterium contents of $x = 1.66, 1.78$ and 1.95 and a mass of about 4 g each were obtained by fixing the deuterium pressure after the pressure-composition-isotherms measurements and cooling down the sample to room temperature.

Powder XRD was measured using a Rigaku 2500V diffractometer in combination with Cu-kα radiation ($\lambda = 0.154$ nm) and with a symmetric $\theta - 2\theta$ scan (Bragg Brentano). The diffraction patterns were analyzed by the Rietveld refinement program RIETAN-2000.$^4$

Neutron diffraction measurements were carried out at the diffractometer NOVA located at the Japan Proton Accelerator Research Complex (J-PARC).$^5$ Powder samples were filled into pure vanadium tubes with an outer diameter of 6.0 mm and a wall thickness of 0.1 mm. The diffraction patterns were analyzed with the Rietveld refinement program Z-Rietveld.
The $^2$H magic angle spinning nuclear magnetic resonance (MAS NMR) measurements were performed with a Bruker Avance 400 spectrometer with a Larmor frequency of 61.423 MHz. Powder samples were filled into zirconia rotors with an outer diameter of 2.5 mm. The NMR spectra were measured with a single pulse sequence and a sample spinning rate of 15 kHz. A 90° pulse of 3.5 $\mu$s in length was used and the recycle delay was set to 1 s. The spectra were referenced to D$_2$O at 0 ppm.
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Figure S1: Spectrum of the Philips MR16 MASTER LEDs (10/50 W) with a color temperature of 4,000 K used for the white-light optical transmission (hydrogenography) measurements.

Figure S2: Photographs of the *in situ* XRD/XRR set-up. (a) Anton Paar XRK900 mounted inside the Bruker D8 Discover diffractometer. (b) Additional adapter plate that can be positioned between the sample insert and the main body of the chamber to allow the samples to be positioned in the center of the goniometer. (c) Sample holders were constructed that allow the samples to be oriented under different tilting angles $\chi$ inside the reactor chamber.
Figure S3: Pressure-composition-isotherm of bulk powder HfD$_x$ measured by stepwise decreasing the deuterium pressure at $T = 300$ °C.
Figure S4: Out-of-plane and in-plane XRD measurements (Cu-Kα λ = 0.1542 nm) on the 60 nm Hf films capped with a 10 nm Pd layer and with a 3 nm Ti adhesion layer at T = 28 °C HfDₓ measured in a plastic Bruker air-tight sample holder containing > 1 atm hydrogen. The sample was tilted perpendicular to the X-ray beam by different angles χ. The X-ray diffraction patterns have been normalized to the larger of 0.4 cps or the maximum intensity and shifted by the values indicated.
Figure S5: Rocking curves of the 60 nm Hf films capped with a 10 nm Pd layer and with a 3 nm Ti adhesion layer measured in air on the HfH$\langle 111 \rangle$ peak ($2\theta$ = 32.9°, $\chi$ = 0°).