The effect of post-process annealing on optical and electrical properties of mixed $\text{HfO}_2\text{--TiO}_2$ thin film coatings

Agata Obstarczyk¹ · Danuta Kaczmarek¹ · Michal Mazur¹ · Damian Wojcieszak¹ · Jaroslaw Domaradzki¹ · Tomasz Kotwica¹ · Jerzy Morgiel²

Received: 5 December 2018 / Accepted: 13 February 2019 / Published online: 26 February 2019
© The Author(s) 2019

Abstract

In this paper a comparison of electrical and optical properties of mixed hafnium-titanium oxides is described. Thin films were deposited with the use of the magnetron co-sputtering method. For further analysis $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$ and $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$ coatings, which were amorphous directly after the deposition process, were chosen. Moreover, post-process annealing was also performed in order to compare the electrical and optical properties of amorphous and nanocrystalline thin films with the same material composition. It was found that the phase transition from amorphous to orthorhombic HfTiO_4 occurred in the case of $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$ coating at 650 °C. In turn, the phase transition to TiO_2 -anatase was observed at the temperature of 600 °C in the case of $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$ thin film. The leakage current for both amorphous coatings was in the range of $10^{-7}\text{--}10^{-8}$ A/cm². After additional annealing and phase transition, the leakage current slightly decreased for $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$ thin film, while in the case of $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$ sample the resistance switching effect was observed. The dielectric constant was equal to 24 and 25 for amorphous $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$ and $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$ films, respectively. However, after the phase transition it decreased to 15 for $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$ and increased to 51 for $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$ film. The results of optical studies showed that amorphous thin films were well transparent in a visible light range with an average transparency of ca. 85%. After the phase transition to HfTiO_4 -orthorhombic and TiO_2 -anatase, a slight decrease in the transparency level by 3% and a redshift of the cut-off wavelength was observed. Moreover, additional annealing caused small changes of the optical band gap energy, refractive index and extinction coefficient.

1 Introduction

Transition metal oxides are the focus of attention due to their outstanding chemical stability and excellent physical properties. Therefore, they are suitable for several industrial applications in the field of electronics and optoelectronics [1]. Hafnium dioxide (HfO_2) has received significant attention in the recent years as a potential replacement for SiO_2 used as the gate dielectric material (high-k oxide) in the complementary metal oxide semiconductor (CMOS) technology [2, 3]. HfO_2 is extremely attractive due to its high dielectric constant ($\epsilon_r \sim 25$), large band offset ($\Delta E_c \sim 1.5$ eV) and

chemical stability with silicon [4–15]. The present CMOS technology requires materials that are thermally stable at the temperatures over 800 °C in the case of gate dielectrics [16]. However, the drawback of HfO_2 is its low crystallization temperature of ca. 200 °C [17], resulting in a large leakage current, high oxygen and impurities penetration, and also defect generation which hinders its integration with traditional CMOS processes [5, 6, 14, 16–22]. Hafnium dioxide occurs in three polymorphs, including monoclinic, tetragonal and cubic phases [5, 15, 23]. The monoclinic structure of HfO_2 is the most thermodynamically stable phase under standard temperature and pressure conditions. At temperatures higher than 1700 °C HfO_2 transforms to the tetragonal phase. The transformation to the cubic polymorph occurs at ~2600 °C [23–26]. One of the effective ways of increasing the crystallization temperature is combining HfO_2 with another complementary gate materials, such as titanium dioxide (TiO_2) [6]. Based on some references from the last ten years [6, 12, 13, 18, 19, 27–31], it can be noted that doping HfO_2 with TiO_2 can lead to receiving a higher dielectric

✉ Agata Obstarczyk
agata.obstarczyk@pwr.edu.pl

¹ Faculty of Microsystem Electronics and Photonics, Wrocław University of Science and Technology, Janiszewskiego 11/17, 50-372 Wrocław, Poland

² Institute of Metallurgy and Materials Science, Polish Academy of Sciences, Reymonta 25, 30-059 Cracow, Poland

constant and improvement of electrical properties. In turn, TiO_2 is an attractive material due to its very high dielectric constant ($\epsilon_r \sim 80\text{--}110$) and high crystallization temperature [6, 13, 22]. Titanium dioxide can occur in different crystal structures of anatase, rutile and brookite, however, only first two ones can find potential applications in industry [3, 32–37]. Moreover, additional annealing of TiO_2 -anatase at the temperature over 700 °C results in irreversible phase transition to the rutile phase [33–35, 38]. Besides, it can be noted that Hf and Ti are both 4-valence elements which would restrain the production of oxygen vacancy, thereby reducing the leakage current density of such mixed oxides [11, 14, 16, 18, 21]. Recently, mixed oxide thin films based on HfO_2 and TiO_2 have attracted a lot of attention due to their potential application in, e.g. metal oxide semiconductor devices, thin film transistors, optical and protective coatings or memory devices [39–42].

However, compared with SiO_2 , the number of defects in the interface between HfO_2 - TiO_2 thin film and Si substrate increases, which causes a remarkable decrease in carrier mobility. In the process of obtaining high quality gate dielectric films, the interface control is very important [5, 7, 12]. Annealing is necessary for the high-k material applied in CMOS processing to reduce defects in films and also to control the growth of an interfacial layer [12, 19]. It is well known that at high temperature annealing hafnium oxide efficiently reduces the traps in dielectric films [25, 43]. Ye et al. [12] showed that the rapid thermal annealing at 600 °C of HfTiO thin films leads to obtaining the largest dielectric constant of 45.9, the lowest leakage current, and the optimized interfacial properties. However, it should be emphasized that currently there are no literature reports which focus simultaneously on the influence of thin film structure on their electrical and optical properties.

In this paper, two sets of mixed oxide thin films based on hafnium and titanium dioxide, i.e. $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$ and $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$, were prepared with the use of magnetron co-sputtering. As-deposited coatings were amorphous and the phase transition to nanocrystalline was obtained by proper post-process annealing. It was found that the annealed $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$ thin film had HfTiO_4 -orthorhombic phase, while $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$ had TiO_2 -anatase phase. Furthermore, electrical and optical properties of amorphous and nanocrystalline samples were compared.

2 Experimental

Mixed HfO_2 - TiO_2 oxide thin films with various material compositions were deposited by the reactive magnetron sputtering method. During the deposition, metallic Hf (99.5% purity) and Ti (99.99% purity) targets were co-sputtered for 180 min in the mixed argon-oxygen ($\text{Ar}:\text{O}_2$ 1:1) atmosphere

with a total gas flow of 24 sccm and the pressure kept at ca. 1.5×10^{-2} mbar. Both targets had the form of metallic discs with a diameter of 30 mm. The magnetrons were powered by MSS2 power supply units (DORA Power System). The distance between the targets and the substrates was equal to 160 mm. The thin films were deposited on fused silica (SiO_2) and silicon substrates of $2 \times 2 \text{ cm}^2$. To determine the electrical properties silicon was the preferred choice as the substrate. However, to assess optical properties fused silica was used. The thickness of as-prepared coatings was investigated using a Talysurf CCI Lite (Taylor Hobson) optical profiler based on the 2D profiles of the surface. This measurement was performed at the thin film-substrate boundary which was created with the use of proper masking during the sputtering process. The thickness of the deposited samples was equal to 660 nm for $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$ and 480 nm for $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$ thin film.

After the deposition process, amorphous coatings were annealed using an RS (80/300/11) Nabertherm tubular furnace equipped with a quartz tube. Due to the large temperature difference in the amorphous to crystalline phase transition of hafnium and titanium oxides, post-process annealing was divided into eight stages with a gradual increase in temperature. Due to the low crystallization temperature of HfO_2 [17], the first stage of annealing was carried out at 200 °C. Then, from the second to the fourth stage, the temperature was increased by 100 °C. To precisely determine the phase transition temperature of the amorphous thin films, the final temperature in the fifth, sixth and seventh stage was increased by 50 °C. In each temperature thin films were annealed for 1 h and afterwards the tubular furnace was cooled down to room temperature without using any additional factors (e.g. liquid nitrogen flow or additional ventilation).

The elemental composition of the thin films was investigated using an FESEM FEI Nova NanoSEM 230 scanning electron microscope equipped with an energy dispersive spectrometer (EDAX Genesis). The EDS detector was calibrated with aluminium and copper samples provided with the device. The ZAF model was used for element analysis and the deconvolution settings were chosen for the smallest error in the quantification of each element. The analysis was performed in perpendicular surface-beam orientation.

Microstructure was assessed with the use of X-ray diffraction (XRD) and transmission electron microscopy (TEM). In the case of XRD measurements, the PANalytical Empyrean PIXel3D diffractometer was employed. The step size was equal to 0.02° in 2θ range, while time-per-step was 5 s. This apparatus was equipped with the $\text{Cu K}\alpha$ X-ray source with a wavelength of $1.5406 \text{ \AA}$, while the analysis of the crystallite size was performed according to the Debye–Scherrer's equation [44] with the aid of MDI JADE 5.0 software. In the case of transmission electron microscopy, the TECNAI G²

FEG Super-Twin (200 kV) microscope was used to evaluate the microstructure of as-deposited and annealed thin films. It was equipped with both side-entry wide angle SIS and on-axis bottom mounted Gatan 2K cameras. For the TEM analysis, thin foils were prepared using a focused ion beam (FIB Quanta 3D system) equipped with an Omniprobe lift-out system.

In order to determine the electrical properties, a series of MOS capacitors were fabricated by the deposition of an Au-top electrode through the shadow mask using electron beam evaporation. During the evaporation process, the pressure inside the vacuum chamber was kept at ca. 7×10^{-5} mbar. Gold pellets of 99.99% purity were used as a base material. The current passing through the hot filament was set to 30 mA providing stable conditions for deposition with a speed rate of ca. 1.1 Å/s. The thickness of the golden pads was set to 100 nm. The high-frequency (1 MHz) C–V curves and leakage current characteristics were measured with the aid of a Keithley SCS4200 semiconductor characterization system and a M100 Cascade Microtech probe station. Electrical characterization was carried out at room temperature in dark conditions.

Optical spectroscopy measurements were performed in the wavelength range of 250–1000 nm using an Ocean Optics QE 65000 spectrophotometer with a coupled deuterium-halogen light source. The analysis carried out based on the obtained data allowed to determine the cut-off wavelength ($\lambda_{\text{cut-off}}$) and optical band gap energy (E_g^{opt}) of as-deposited and annealed thin films. The refractive index (n) and extinction coefficient (k) spectral characteristics of the films were determined by the reverse engineering method using FTG FilmStar software employing a generalized Cauchy model.

3 Results and discussion

The amount of titanium in the as-deposited mixed oxide thin films was equal to 48 at% and 71 at%. The EDS spectra showing the lines from titanium (Ti K_α and Ti K_β) and hafnium (Hf L_α , Hf L_β and Hf L_1) elements are presented in Fig. 1.

The diffraction patterns of as-deposited and annealed coatings are shown in Fig. 2. It was found that in the case of as-prepared (Hf_{0.52}Ti_{0.48})Ox and (Hf_{0.29}Ti_{0.71})Ox samples only broad, amorphous-like patterns without peaks related to the crystal phases were visible. Ye et al. [12] showed that the addition of TiO₂ to HfO₂ caused an increase in crystallization temperature (> 700 °C) and improved the microstructure and electrical properties. The amorphous phase is desirable as a potential high- k gate dielectrics in CMOS device application in which leakage current is lower and hence suitable for device application [1].

Fig. 1 EDS spectra of as-deposited HfO₂–TiO₂ thin films

In the case of thin films with 48 at% Ti the phase transition to orthorhombic HfTiO₄ phase occurred at 650 °C. The occurrence of the HfTiO₄ phase was confirmed by the small diffraction peak of weak intensity from the (111) crystal plane. Such orthorhombic-HfTiO₄ crystal phase can occur only at the specified range of the Ti–Hf ratio, i.e. for compounds where titanium content is higher than 36 at% and lower than 53 at% [25, 46]. Further annealing of (Hf_{0.52}Ti_{0.48})Ox coating at 700 °C caused complete crystallization with peaks related to other HfTiO₄ crystal planes. According to the powder diffraction file PDF (40-0794) [45], all peak positions of HfTiO₄ thin film correspond to the orthorhombic phase. The peak intensity from the (111) crystal plane is the strongest for the film annealed at 700 °C (Fig. 2a). In the case of the film with a higher amount of Ti (71 at%) the phase transition occurred at 600 °C. The diffraction peak in Fig. 2b from the (101) crystal plane is in good agreement with the reference value, indicating that the annealed thin film had an anatase phase. Further annealing of (Hf_{0.29}Ti_{0.71})Ox coating at 650 °C and 700 °C did not lead to the phase transition from the anatase to rutile phase or into the mixed anatase–rutile phase system. The average crystallite size was calculated using the following Scherrer's formula [44]:

$$D_{hkl} = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where D_{hkl} is the average crystallite size, $k \sim 0.89$ (close to unity) is the shape factor, λ is the wavelength of X-ray, β is full width at half maximum, and θ is a diffraction angle.

Fig. 2 XRD measurement results of as-deposited and annealed **a** $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$, **b** $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$ thin films

For the annealed $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$ thin film at 650 °C (Fig. 2a) weak and wide diffraction line was observed, which testified about the nanocrystalline nature of the coating. The average crystallites size was ca. 16 nm. Additional annealing at 700 °C caused an improvement of the crystallinity of the film which resulted in the occurrence of more intense and narrower diffraction peaks (Fig. 2a). An increase in the annealing temperature to 700 °C caused a rather negligible increase in the average crystallite size by about 9% (up to 17.4 nm). In the case of $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$ thin film with an anatase structure, after the phase transition at 600 °C it was composed of crystallites with the size of ca. 25.6 nm. However, an increase in the annealing temperature to 650 °C and 700 °C caused a rise in an average crystallite size by about 0.5 nm and 1.7 nm, respectively. Additional annealing caused the occurrence of tensile stress in $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$ and $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$. The type of stress occurring in the annealed coatings was determined on the basis of Δd parameter from the following equation [40, 47, 48]:

$$\Delta d = \left(\frac{d - d_{\text{PDF}}}{d_{\text{PDF}}} \right) \cdot 100\% \quad (2)$$

where d —measured interplanar distance in the thin film; d_{PDF} —standard interplanar distance from the JCPDS powder diffraction file.

Compressive or tensile stresses occur in thin films if Δd parameter is lower or higher than zero, respectively. In the case of thin films after post-process annealing, the XRD analysis showed a significant shift of the measured diffraction peaks towards lower angles, thus revealing the presence of tensile stresses. In the case of the crystalline film with TiO_2 -anatase phase, the tensile stress was

almost two times higher as-compared to the film with the orthorhombic- HfTiO_4 structure. Table 1 summarizes the analysis of the XRD measurement results.

XRD studies confirmed that post-process annealing of amorphous mixed HfO_2 - TiO_2 thin films with different material composition strongly affects their microstructure. The microstructure observations performed with the use of TEM in the bright field mode (BF TEM) of as-deposited $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$ and $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$ coatings and the analysis of electron diffractions (Fig. 3a), which consisted of only fuzzy rings, confirmed that films were amorphous. As a result of the occurrence of the amorphous phase in as-deposited coatings a halo was left around the bright center spot in the electron diffraction patterns. Such an image is the result of random scattering of electrons by the amorphous structure and it is a common method in the identification of glassy and amorphous materials. TEM studies also showed that thin films with 48 and 71 at% of titanium were densely packed, with a very smooth surface, negligible roughness and without visible voids.

The change in the microstructure of amorphous thin films $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$ and $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$ with the increase in temperature was also observed during *in-situ* measurements conducted using a transmission electron microscope. These studies showed that the crystallization proceeded through the growth of a crystal nucleus. The growth of nanocrystals was similar to the dendritic growth, i.e. the propagation of crystallization occurred in different directions. In the case of the $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$ thin film, the temperature at which the phase transformation occurred was about 650 °C, while for the $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$ film the temperature of the phase change was lower and equal to ca. 600 °C. As the crystallization temperature was kept at the same level, the crystalline phase growth was faster and nucleation began also in other places.

Table 1 XRD measurement results of as-deposited and annealed $\text{HfO}_2\text{--TiO}_2$ thin films

Thin film	Crystal structure	D (nm)	d (nm)	d_{PDF} (nm)	Δd (%)	Type of stress
$(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$						
As-deposited	Amorphous	—	—	—	—	—
Annealed 200–600 °C						
Annealed 650 °C	HfTiO_4 orthorhombic	16.0	0.2958	0.2935 [45]	+ 0.78	Tensile
Annealed 700 °C		17.4	0.2953		+ 0.61	Tensile
$(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$						
As-deposited	Amorphous	—	—	—	—	—
Annealed 200–550 °C						
Annealed 600 °C	TiO_2 anatase	25.6	0.3564	0.3520 [49]	+ 1.25	Tensile
Annealed 650 °C		26.1	0.3568		+ 1.36	Tensile
Annealed 700 °C		27.3	0.3565		+ 1.28	Tensile

Designations: D, calculated average crystallite size according to the Scherrer's equation; d, measured interplanar distance; Δd , percentage change of the measured interplanar distance as-compared to the standard one (d_{PDF}) [45, 49]

Fig. 3 BF TEM image with electron diffraction from SAED for $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$ and $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$ thin films: **a** as-deposited, **b** annealed after phase transition

Figure 3b shows bright field images with electron diffraction for annealed $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$ and $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$ thin films. The BF TEM observations (Fig. 3b) of coatings after the phase transition showed visible voids (places with a much lighter contrast). The occurrence of voids in the annealed thin films can be explained by the difference in the density of the amorphous and crystalline material, where the crystalline area is denser than the amorphous one. With the growth of the crystalline phase, the density of the film increases locally, which leads to the formation of voids and pores in other places. The analysis of bright field images and electron

diffractions confirmed that the nanocrystalline phase in the annealed $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$ films was orthorhombic HfTiO_4 , while for $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$ films it was TiO_2 -anatase phase. Electron diffractions had an almost spotted character that can indicate the occurrence of the highly crystalline microstructure of the samples and that its crystallite sizes are rather large. The electron diffraction analysis for the film with 71 at% of titanium confirmed that this coating had an TiO_2 -anatase phase with the [010] zone axis.

In order to confirm the observations in the bright field mode the high resolution transmission electron microscope

(HRTEM) measurements were also performed. The analysis of HRTEM studies with Fourier transforms (attached as insets to the HRTEM images in Figs. 4a, 5a) confirmed that as-deposited films were entirely amorphous.

The HRTEM image with Fourier diffraction patterns (FFT) for annealed ($\text{Hf}_{0.52}\text{Ti}_{0.48}\text{Ox}$) film is shown in Fig. 4b as an inset. These observations confirmed that the entire coating is very well crystallized at the silicon substrate, in the centre part and on the surface. Figure 4b shows that the crystal planes correspond to the HfTiO_4

orthorhombic phase. For the determined interplanar distances and angles, the $[1\bar{1}2]$ (Fig. 4b) zone axis was calculated.

Figure 5b shows the HRTEM image for ($\text{Hf}_{0.29}\text{Ti}_{0.71}\text{Ox}$) thin film annealed at 600 °C. In this case, the coating was also very well crystallized in its entire volume. The HRTEM image again did not confirm the occurrence of the amorphous phase. The low-index planes were marked in the HRTEM image (Fig. 5b). The $\bar{1}01$ zone axis (Fig. 5b) was determined. The HRTEM images and FFT diffraction

Fig. 4 TEM investigation results: **a** HRTEM image with FFT inset for as-deposited ($\text{Hf}_{0.52}\text{Ti}_{0.48}\text{Ox}$) film, **b** HRTEM image with FFT inset for annealed at 650 °C ($\text{Hf}_{0.52}\text{Ti}_{0.48}\text{Ox}$) film

Fig. 5 TEM investigation results: **a** HRTEM image with FFT inset for as-deposited ($\text{Hf}_{0.29}\text{Ti}_{0.71}\text{Ox}$) film and **b** HRTEM image with FFT inset for annealed at 600 °C ($\text{Hf}_{0.29}\text{Ti}_{0.71}\text{Ox}$) film

patterns analysis for film with 71 at% of titanium confirmed that this coating had an TiO_2 -anatase phase.

The influence of the phase transition from amorphous to the crystalline after post process annealing of $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$ and $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$ thin films on electrical properties was also investigated (Table 2). It was found that in the case of the as-deposited film containing 48 at% of Ti, the electrical resistivity was at the same order as for HfTiO_4 -orthorhombic film after the phase transition, and equal to $5.5 \times 10^{10} \Omega \text{ cm}$. In turn, for coating with 71 at% of Ti its resistivity value increased over 4.5 times (up to $\rho \sim 3.43 \times 10^{10} \Omega \text{ cm}$) after annealing and phase transition.

The I–V characteristics of the prepared and annealed thin films are shown in Fig. 6. The values of the leakage current density was evaluated by the determination of the lowest

point at the I–V characteristic according to the standard method used for the determination of the leakage current for junction based devices [e.g. 50, 51]. Leakage current density for amorphous coatings was in the range of 10^{-7} – 10^{-8} A/cm^2 and the lowest value was equal to $5.02 \times 10^{-8} \text{ A/cm}^2$ for $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$ thin film. The obtained values of the leakage current density for prepared amorphous films were in good agreement with the literature data, e.g. [3, 6, 13]. According to Honda et al. [3] leakage current density was in the order 10^{-9} A/cm^2 for amorphous HfO_2 - TiO_2 composite film with 10 at% TiO_2 . However, Zhang et al. [13] showed that the lowest leakage current density was obtained for TiO_2 -doped HfO_2 films annealed at 400°C , and was equal to $5.4 \times 10^{-5} \text{ A/cm}^2$. On the other hand, Ye et al. [12] showed that annealing at 500°C leads to obtaining the

Table 2 Influence of phase transition on electrical parameters of mixed HfO_2 - TiO_2 thin films

Thin film	Crystallization temperature ($^\circ\text{C}$)	Crystal structure	ρ ($\Omega \text{ cm}$)	j_u (A/cm^2)	ϵ_r
$(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$	–	Amorphous	5.62×10^{10}	1.60×10^{-7}	24
	650	HfTiO_4 (orthorhombic)	5.25×10^{10}	–	15
$(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$	–	Amorphous	7.65×10^9	5.02×10^{-8}	25
	600	TiO_2 (anatase)	3.34×10^{10}	3.48×10^{-8}	51

Designations: ρ , electrical resistivity; j_u , leakage current density; ϵ_r , dielectric constant

Fig. 6 Current–voltage (I–V) characteristics for: **a, c** as-deposited and **b, d** annealed (after phase transition) $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$ and $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$ thin films

lowest leakage current density equal to 1.81×10^{-7} A/cm² for amorphous HfTiO films. Jiang et al. [6] compared amorphous HfTiO films deposited by magnetron sputtering at different working pressures and reported that the lowest leakage current density was equal to 1.39×10^{-5} A/cm² for films deposited at 0.6 Pa. Concerning the structure, such amorphous layers are desirable in MOS technology. Thin films with 48 at% of Ti had a crystalline, orthorhombic HfTiO₄ structure after phase transition at 650 °C. After annealing of (Hf_{0.52}Ti_{0.48})O_x film, the resistance switching effect was observed (Fig. 6b) [52, 53]. Therefore, the determination of the influence of the phase change on the leakage current density in the prepared thin films was possible only in the case of the coating with TiO₂-anatase structure (Table 2). For the crystalline (Hf_{0.29}Ti_{0.71})O_x film the value of the leakage current density was equal to 3.48×10^{-8} A/cm², therefore a significant decrease was observed after phase transition. Lee et al. [54] showed that the value of the leakage current density for the amorphous and nanocrystalline HfO₂ was almost the same, and therefore no conductivity along the grain boundaries was observed. It should be emphasized that currently there are no literature reports which focus on thin films based on Hf and Ti oxides with an amorphous and nanocrystalline HfTiO₄-orthorhombic and TiO₂-anatase structure. In Fig. 6a, c, d two regions could be distinguished in I–V characteristics. The first region with voltage up to

0.5 V (in Fig. 6d up to 0.2 V) is characterized by a nearly linear current-to-voltage dependence and can be connected with the leakage current region in the thin film. The second region with voltage value above 0.5 V (in Fig. 6 d above the 0.2 V) may be connected with the space-charge limited current (SCLS) conduction. Moreover, Fig. 6d showed the characteristic shift indicating the presence of a built-in charge in the crystalline TiO₂-anatase film after annealing at 600 °C. The cause of the occurrence of the built-in charge may be related to various types of electrically charged active defects, e.g. grain boundaries.

High frequency (1 MHz) C–V characteristics for as-deposited and annealed thin films are presented in Fig. 7. Dielectric constant (ϵ_r) for amorphous coatings was estimated from the measured capacitance in the accumulation state shown in Fig. 7a, c. It was found that ϵ_r was equal to 24 and 25 for (Hf_{0.52}Ti_{0.48})O_x and (Hf_{0.29}Ti_{0.71})O_x films, respectively (Table 2). According to the literature [6, 11, 18] in mixed HfO₂ and TiO₂ films, it is possible to obtain a material with modified values of the dielectric constant in a wide range, however, the most suitable value of ϵ_r for high-k oxides is in the range from 25 to 35 [9, 15]. Jiang and others [6] showed that for films based on a mixture of Hf and Ti oxides with an amorphous phase, the values of ϵ_r were in the range from 29 to 39. Table 2 shows the influence of the phase transition of (Hf_{0.52}Ti_{0.48})O_x and (Hf_{0.29}Ti_{0.71})

Fig. 7 High frequency (1 MHz) capacitance–voltage (C–V) curves for: **a, c** as-deposited and **b, d** annealed (after phase transition) (Hf_{0.52}Ti_{0.48})O_x and (Hf_{0.29}Ti_{0.71})O_x thin films

Ox on the dielectric constant. The results revealed that the phase change after post-process annealing caused significant changes in the dielectric constant. In the case of the thin film with 48 at% of Ti with the HfTiO_4 -orthorhombic phase after annealing at 650 °C the dielectric constant decreased from 24 to 15. However, for crystalline $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$ film with TiO_2 -anatase structure, this parameter increased over two times in relation to the film with an amorphous phase, and was equal to 51. Ye et al. [12] showed that the phase transition from amorphous to monoclinic structure for mixed HfO_2 and TiO_2 films occurred at 700 °C. It was found that after annealing the dielectric constant decreased from 34 to 19, for amorphous and monoclinic structure, respectively.

The optical properties of as-deposited and annealed thin films after their phase transition were determined based on optical transmission (T_λ) measurements. The results of these measurements of $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$ and $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$ coatings are presented in Fig. 8. The as-deposited samples with an amorphous phase were transparent in the visible wavelength range with the transmission of approximately 86% and 85% for $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$ and $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$, respectively. After the phase transition of amorphous films to HfTiO_4 -orthorhombic and TiO_2 -anatase, a slight decrease in the transparency level was observed to 83% and 82%, respectively.

Figure 8 shows the results of the determination of the fundamental absorption edge (λ_{cutoff}) position for as-deposited and annealed coatings. For as-deposited $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$ and $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$ thin films the cut-off wavelength was equal to 296 nm and 319 nm, respectively. After annealing, only a slight redshift of the cut-off wavelength of a few nanometers was observed (Fig. 8).

Fig. 8 Optical transmission spectra with marked position of the fundamental absorption edge (λ_{cutoff}) for as-deposited and annealed $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$ and $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$ thin films

It is well known that HfO_2 and TiO_2 are both indirect band gap insulators, so the mixed HfO_2 - TiO_2 film can be also regarded as an indirect allowed transition material [1, 19, 22, 40, 41, 53]. The Tauc plots were used to assess the optical band gap energy of the deposited and annealed thin films, which was determined for indirect transitions [55–57]. A plot of $(\alpha h\nu)^{1/2}$ vs $(h\nu)$ is shown in Fig. 9 and the linear portion of the curve was extrapolated to the energy axis to determine the optical band gap energy. The obtained E_g^{opt} values for amorphous films were equal to 3.54 eV and 3.37 eV for $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$ and $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$, respectively. According to the literature [6, 11, 18, 22, 29, 40, 41, 56], thin films based on a mixture of two oxides with significantly different values of band gap energy (with a wide and narrow energy gap) can be a material with a modified (tailored) value of this parameter. Jiang and others [6] showed that for mixed HfO_2 - TiO_2 thin films with an amorphous phase, the values of E_g^{opt} were in the range from 3.59 to 3.77 eV. The phase transition after the annealing process for $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$ films caused a decrease in the E_g^{opt} from 3.54 eV to 3.50 eV. In the case of the annealed thin film with a higher amount of Ti with the anatase structure, the value of this parameter was also reduced to 3.34 eV (Fig. 9).

Based on the measured characteristics of optical transmission (Fig. 8), the reverse engineering method was employed with the use of FilmStar software and the Generalized Cauchy model to determine the refractive index and extinction coefficient. The n and k characteristics in the wavelength function were plotted in Fig. 10. It was found that the values of the refractive index for as-deposited $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$ and $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$ films at 550 nm were equal to 1.84 and 1.98, respectively. The results revealed that the phase change after post-process annealing caused a slight change in the values of refractive index in the range of 1.0–1.6% (Fig. 10a). In the

Fig. 9 Results of optical band gap energy for as-deposited and annealed $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$ and $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$ thin films

Fig. 10 Results of optical parameters: **a** refractive index, **b** extinction coefficient for as-deposited and annealed $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$ and $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$ thin films

case of the crystalline thin film with HfTiO_4 -orthorhombic and TiO_2 -anatase phases, the refractive index decreased from 1.84 to 1.81 and from 1.98 to 1.96, respectively. As it was stated in the TEM results part, the bright field observations of both annealed films showed the presence of voids and pores in places with a much lighter contrast. A local decrease in the density of the thin films and the introduction of such microstructural defects resulted in a slight decrease in the refractive index.

The analysis of the extinction coefficient for amorphous and nanocrystalline $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$ and $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$ films after the phase change showed that this parameter increased twice in both cases (Fig. 10b). Unfortunately this fact is disadvantageous, because it is directly related to the higher absorption and scattering of light in crystalline thin films. However, according to the Nair et al. [47] the low value of the extinction coefficient of the order of 10^{-2} is a qualitative indication of the excellent surface smoothness of the prepared samples. The results of the influence of the

phase transition on optical parameters of $(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$ and $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$ films are summarized in Table 3.

4 Conclusion

In this paper, mixed hafnia (HfO_2) and titania (TiO_2) thin films, deposited by reactive magnetron sputtering with different material compositions were described. In the case of structural properties, XRD and TEM studies revealed that as-deposited films with 48 and 71 at% of Ti were amorphous. Additionally, amorphous coatings were annealed to compare films with the same material composition but with the different type of the structure. In the case of the thin film with 48 at% Ti the phase transition to orthorhombic HfTiO_4 phase occurred at 650 °C and the crystallites size was equal to 16.0 nm. In turn, $(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$ coating after the phase transition at 600 °C was composed of crystallites in the size of ca. 25.6 nm of the anatase phase.

Table 3 Influence of phase transition on optical parameters of mixed HfO_2 - TiO_2 thin films

Thin film	Crystallization temperature	Crystal structure	T_λ (%)	λ_{cutoff} (nm)	E_g^{opt} (eV)	n	k
$(\text{Hf}_{0.52}\text{Ti}_{0.48})\text{Ox}$	—	Amorphous	86	296	3.54	1.84	2.64×10^{-3}
	650 °C	HfTiO_4 (orthorhombic)	83	300	3.50	1.81	5.25×10^{-3}
$(\text{Hf}_{0.29}\text{Ti}_{0.71})\text{Ox}$	—	Amorphous	85	319	3.37	1.98	2.56×10^{-3}
	600 °C	TiO_2 (anatase)	82	324	3.34	1.96	5.78×10^{-3}

Designations: T_λ , optical transmission; λ_{cutoff} , fundamental absorption edge; E_g^{opt} , optical band gap energy; n, refractive index; k, extinction coefficient

The measurements of electrical properties revealed that resistivity for amorphous and crystalline ($\text{Hf}_{0.52}\text{Ti}_{0.48}\text{Ox}$) film was very similar and equal to ca. $5 \times 10^{10} \Omega \text{ cm}$. In the case of the coating with 71 at% of Ti, its resistivity value after the phase transition increased over 4.5 times to $3.34 \times 10^{10} \Omega \text{ cm}$. Leakage current density for both amorphous coatings was in the range of 10^{-7} – 10^{-8} A/cm^2 and the lowest value was determined for the film with 71 at% of Ti. Moreover, after the phase transition of ($\text{Hf}_{0.52}\text{Ti}_{0.48}\text{Ox}$) film the resistance switching effect was observed. The dielectric constant was equal to 24 and 25 for amorphous ($\text{Hf}_{0.52}\text{Ti}_{0.48}\text{Ox}$) and ($\text{Hf}_{0.29}\text{Ti}_{0.71}\text{Ox}$) films, respectively. However, after the transition to the crystalline phase the dielectric constant significantly decreased to 15 for ($\text{Hf}_{0.52}\text{Ti}_{0.48}\text{Ox}$) thin film and increased to 51 for ($\text{Hf}_{0.29}\text{Ti}_{0.71}\text{Ox}$) coating.

The results of optical studies showed that amorphous films were well transparent in a visible light range with the average transmission (at $\lambda = 550 \text{ nm}$) of approximately 86% and 85% for ($\text{Hf}_{0.52}\text{Ti}_{0.48}\text{Ox}$) and ($\text{Hf}_{0.29}\text{Ti}_{0.71}\text{Ox}$), respectively. After the phase transition, only a slight decrease (ca. 3%) in the transparency level was observed for both samples. The cut-off wavelength for amorphous ($\text{Hf}_{0.52}\text{Ti}_{0.48}\text{Ox}$) film was equal to 296 nm, while for the film with higher Ti content (71 at%) it was shifted towards longer wavelength, i.e. 319 nm. After annealing, only a negligible redshift of the cut-off wavelength was observed for nanocrystalline coatings. It was found that optical band gap energy (E_g^{opt}) for amorphous films was equal to 3.54 eV and 3.37 eV for film with 48 and 71 at% of Ti, respectively. After post-process annealing, the value of E_g^{opt} parameter was reduced in each case by at most 0.03–0.04 eV. It was found that the refractive index for as-deposited ($\text{Hf}_{0.52}\text{Ti}_{0.48}\text{Ox}$) and ($\text{Hf}_{0.29}\text{Ti}_{0.71}\text{Ox}$) films was equal to 1.84 and 1.98, respectively. However, after post-process annealing a slight decrease was observed. The analysis of the extinction coefficient for amorphous and nanocrystalline films after the phase transition showed that this parameter increased twice in both cases.

The best electrical and optical properties were obtained for amorphous ($\text{Hf}_{0.29}\text{Ti}_{0.71}\text{Ox}$) coating. Due to the presented properties, it could be used as, e.g. an insulating layer in CMOS structures (with properly selected thickness) and also as an optical layer for optoelectronics application. After the phase transition, the electrical and optical properties were still very favorable. Therefore, this thin film could be used in high-temperature electronics.

Acknowledgements This work was co-financed by the Polish National Science Centre (NCN), under research Project Number DEC-2013/09/B/ST8/00140 and from statutory sources 0401/0130/18.

Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate

credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

1. J. Gao, G. He, B. Deng, D.Q. Xiao, M. Liu, P. Jin, C.Y. Zheng, Z.Q. Sun, *J. Alloys Compd.* **662**, 339 (2016)
2. F.M. Li, B.C. Bayer, S. Hofmann, J.D. Dutson, S.J. Wakeham, M.J. Thwaites, W.I. Milne, A.J. Flewitt, *Appl. Phys. Lett.* **98**, 252903 (2011)
3. K. Honda, A. Sakai, M. Sakashita, H. Ikeda, S. Zaima, Y. Yasuda, *Jpn. J. Appl. Phys.* **43**, 1571 (2004)
4. C.H. Fu, K.S. Chang-Liao, Y.A. Chang, Y.Y. Hsu, T.H. Tzeng, T.K. Wang, D.W. Heh, P.Y. Gu, M.J. Tsai, *Microelectron. Eng.* **88**, 1309 (2011)
5. J. Gao, G. He, J.W. Zhang, B. Deng, Y.M. Liu, *J. Alloys Compd.* **647**, 322 (2015)
6. S.S. Jiang, G. He, J. Gao, D.Q. Xiao, P. Jin, W.D. Li, J.G. Lv, M. Liu, Y.M. Liu, Z.Q. Sun, *Ceram. Int.* **42**, 11640 (2016)
7. A.G. Khairnar, A.M. Mahajan, *Solid State Sci.* **15**, 24 (2013)
8. H. Kim, P.C. McIntyre, C.O. Chui, K.C. Saraswat, S. Stemmer, *J. Appl. Phys.* **96**, 3467 (2004)
9. J. Robertson, R.M. Wallace, *Mater. Sci. Eng. R* **88**, 1 (2015)
10. J.F. Wager, D.A. Keszler, R.E. Presley, *Transparent Electronics* (Springer, New York, 2008)
11. C. Ye, H. Wang, J. Zhang, Y. Ye, Y. Wang, B. Wang, Y. Jin, *J. Appl. Phys.* **107**, 1 (2010)
12. C. Ye, C. Zhan, J. Zhang, H. Wang, T. Deng, S. Tang, *Microelectron. Reliab.* **54**, 388 (2014)
13. J.W. Zhang, G. He, H.S. Chen, J. Gao, X.F. Chen, P. Jin, D.Q. Xiao, R. Ma, M. Liu, Z.Q. Sun, *J. Alloys Compd.* **647**, 1054 (2015)
14. J.W. Zhang, G. He, L. Zhou, H.S. Chen, X.S. Chen, X.F. Chen, B. Deng, J.G. Lv, Z.Q. Sun, *J. Alloys Compd.* **611**, 253 (2014)
15. H. Zhu, C. Tang, L.R.C. Fonseca, R. Ramprasad, *J. Mater. Sci.* **47**, 7399 (2012)
16. S. Pokhriyal, S. Biswas, *Nanopart. Mater. Today Proceed.* **3**, 1311 (2016)
17. V. Kolkovsky, K. Lukat, E. Kurth, C. Kunath, *Solid State Electron.* **106**, 63 (2015)
18. P. Jin, G. He, M. Liu, D.Q. Xiao, J. Gao, X.F. Chen, R. Ma, J.W. Zhang, M. Zhang, Z.Q. Sun, Y.M. Liu, *J. Alloys Compd.* **649**, 128 (2015)
19. P. Jin, G. He, P.H. Wang, M. Liu, D.Q. Xiao, J. Gao, H.S. Chen, X.S. Chen, Z.Q. Sun, M. Zhang, J.G. Lv, Y.M. Liu, *J. Alloys Compd.* **688**, 925 (2016)
20. N. Manikantababu, M. Dhanunjaya, S.V.S. Nageswara Rao, A.P. Pathak, *Nucl. Instrum. Methods* **379**, 230 (2016)
21. J. Zhang, Z. Li, H. Zhou, C. Ye, H. Wang, *Appl. Surf. Sci.* **294**, 58 (2014)
22. J.W. Zhang, G. He, M. Liu, H.S. Chen, Y.M. Liu, Z.Q. Sun, X.S. Chen, *Appl. Surf. Sci.* **346**, 489 (2015)
23. J.C. Garcia, A.T. Lino, L.M.R. Scolfaro, J.R. Leite, V.N. Freire, G.A. Farias, E.F. da Silva Jr., *Phys. Semicond.* **772**, 189 (2005)
24. M. Vargas, N.R. Murphy, C.V. Ramana, *Opt. Mater.* **37**, 621 (2014)
25. J. Wang, H.P. Li, R. Stevens, *J. Mater. Sci.* **27**, 5397 (1992)
26. Y.L. Yang, X.L. Fan, C. Liu, R.X. Ran, *Phys. B* **434**, 7 (2014)
27. K.S. Chang, W.C. Lu, C.Y. Wu, H.C. Feng, *J. Alloys Compd.* **615**, 386 (2014)
28. M.C. Cisneros-Morales, C.R. Aita, *J. Vac. Sci. Technol. A* **28**, 1161 (2010)
29. G. He, X.F. Chen, J.G. Lv, Z.B. Fang, Y.M. Liu, K.R. Zhu, Z.Q. Sun, M. Liu, *J. Alloys Compd.* **642**, 172 (2015)

30. M. Liu, L.D. Zhang, G. He, X.J. Wang, M. Fang, J. Appl. Phys. **108**, 1 (2010)
31. J.W. Zhang, G. He, M. Liu, J. Gao, P.H. Wang, S.W. Shi, M. Zhang, H.S. Chen, Y.M. Liu, Z.Q. Sun, J. Alloys Compd. **646**, 10 (2015)
32. O. Carp, C.L. Huisman, A. Reller, Prog. Solid State Chem. **32**, 33 (2004)
33. U. Diebold, Surf. Sci. Rep. **48**, 53 (2003)
34. D.A.H. Hanaor, C.C. Sorrell, J. Mater. Sci. **46**, 855 (2011)
35. N. Rahimi, R.A. Pax, E.M.A. Gray, Prog. Solid State Chem. **44**, 86 (2016)
36. W. Trzebiatowski, *Chemia nieorganiczna* (Państwowe Wydawnictwo Naukowe, Warszawa, 1965)
37. D.J. Won, C.H. Wang, H.K. Jang, D.J. Choi, Appl. Phys. **73**, 595 (2001)
38. Y.Q. Hou, D.M. Zhuang, G. Zhang, M. Zhao, M.S. Wu, Appl. Surf. Sci. **218**, 97 (2003)
39. N.W. Pi, M. Zhang, J. Jiang, A. Belosludtsev, J. Vlček, J. Houška, E.I. Meletis, Thin Solid Films **619**, 239 (2016)
40. M. Mazur, D. Kaczmarek, J. Domaradzki, D. Wojcieszak, A. Poniedziałek, Coatings **6**, 1 (2016)
41. M. Mazur, A. Poniedziałek, D. Kaczmarek, D. Wojcieszak, J. Domaradzki, D. Gibson, Appl. Surf. Sci. **421**, 170 (2017)
42. M. Mazur, D. Wojcieszak, J. Domaradzki, D. Kaczmarek, A. Poniedziałek, P. Domanowski, Mater. Res. Bull. **72**, 116 (2015)
43. V. Singh, S.K. Sharma, D. Kumar, R.K. Nahar, Microelectron. Eng. **91**, 137 (2012)
44. H.P. Klug, E.E. Alexander, *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, 2nd edn. (Wiley, New York, 1974)
45. Powder Diffraction File, Joint Committee on Powder Diffraction Standards, ASTM, Philadelphia, PA, PDF Card 40-0794
46. R. Ruh, G.W. Hollenberg, E.G. Charles, V.A. Patel, J. Am. Ceram. Soc. **59**, 495 (1976)
47. P.B. Nair, V.B. Justinivictor, G.P. Daniel, K. Joy, V. Ramakrishnan, P.V. Thomas, Appl. Surf. Sci. **257**, 10869 (2011)
48. S. Jena, R.B. Tokas, J.S. Misal, K.D. Rao, D.V. Udupa, S. Thakur, N.K. Sahoo, Thin Solid Films **592**, 135 (2015)
49. Powder Diffraction File, Joint Committee on Powder Diffraction Standards, ASTM, Philadelphia, PA, PDF Card 21-1276
50. S. Das, K. Gosh, R. Sarkar, S. Dutta, S. Mukherjee, S. Ganguly, A. Laha, Epitaxial lanthanide oxide on III-Nitride substrates for high power MOS HEMT application, in *Conference Paper WOCSDICE 2017* (Las Palmas de Gran Canaria, Spain, 2017)
51. J.D. Servaites, M.A. Ratner, T.J. Marks, Organic solar cells: a new look at traditional models. Energy Environ. Sci. **4**, 4410 (2011). <https://doi.org/10.1039/c1ee01663>
52. M. Lanza, Mater. **7**, 2155 (2014)
53. H.Z. Zhang, D.S. Ang, K.S. Yew, X.P. Wang, IEEE Electron Device Lett. **37**, 1116 (2016)
54. B.H. Lee, L. Kang, R. Nieh, W.J. Qi, J.C. Lee, Appl. Phys. Lett. **76**, 1926 (2000)
55. J.W. Zhang, G. He, J. Gao, X.S. Chen, X.F. Chen, B. Deng, Y.M. Liu, M. Zhang, J.G. Lv, Z.Q. Sun, Sci. Adv. Mater. **6**, 1979 (2014)
56. V. Dave, H.O. Gupta, R. Chandra, Appl. Surf. Sci. **295**, 231 (2014)
57. J. Domaradzki, *Powłoki optyczne na bazie TiO₂* (Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław, 2010)

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.