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Structure and optical properties of HfO_2 films on Si (100) substrates prepared by ALD at different temperatures

Sai Li [a], Yong Zhang [b], Dewei Yang [a], Wen Yang [a], Xiaobo Chen [c], Hengli Zhao [a], Jing Hou [a], Peizhi Yang [a,*]

[a] Key Laboratory of Advanced Technique & Preparation for Renewable Energy Materials, Ministry of Education, Yunnan Normal University, Kunming, 650092, China
[b] Department of Electrical and Computer Engineering and Center for Optoelectronics, University of North Carolina at Charlotte, 9201 University City Blvd Charlotte, NC, 28223, USA
[c] School of Physics and Electronic Engineering, Yancheng Teachers University, Yancheng, 224051, PR China

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A B S T R A C T

In this work, HfO_2 thin films were deposited on Si (100) wafer by using reactive atomic layer deposition at different temperatures. By characterizing the Raman spectroscopy and XRD patterns, we find that with the substrate temperature increases, the structure of the film transforms continuously, and a substrate with sufficiently high temperature can generate enough energy to produce a film in the crystalline phase. UV–vis absorption spectrum shows that the anti-reflection effect of the deposited HfO_2 thin films is effective. The characteristic reflective peak of the film exhibits a slightly blue shift with increasing the substrate temperature, indicating that the thickness of the film decreases as the substrate temperature increases. The refractive index of the visible to near infrared spectral range increases with the increase of temperature, and the film becomes more compact. The surface morphology of HfO_2 films was measured by AFM, and the skewness, kurtosis and roughness of the films were also analysed. Increasing substrate temperature has led to improvement in the film uniformity and compactness. The above results indicate that the substrate temperature is a critical parameter in determining the film structure, morphology and optical properties.

1. Introduction

In recent years, HfO_2 has attracted more and more attention due to its unique properties and important technical applications. HfO_2 is an excellent material due to the following characteristics, such as large band gap, high dielectric constant, superior surface passivation performance, high refractive index, good stability [1,2], wide range of UV-IR transparency region, and high laser damage threshold (LDT) etc. [3]. In addition, HfO_2 films are widely used in various electronic and optical fields because of its unique structure, optical and electrical properties. Moreover, in the field of optics application, HfO_2 film has a good anti-reflection performance in some optical devices, which can effectively reduce the Fresnel loss [4]. It is widely used in optical coatings due to its high refractive index and excellent transmittance [5]. However, optical applications require uniform, smooth, dense and stoichiometric films, especially in the ultraviolet spectral region. The reflection is the intrinsic mechanism of the optical loss in the transparent region of the material, and the extrinsic causes of optical losses may include surface roughness, impurities, film composition and structure nonuniformity. Therefore, it is significant to prepare high-purity, high-quality and stoichiometric films and to perform high-performance control of components under various conditions. How to make the high-quality growth and optimization of HfO_2 film become an urgent need for development.

A fact is that the structural and optical properties of HfO_2 thin films are highly dependent on the thin film deposition technology. So far, there are multiple conventional ways to deposit HfO_2 thin films, such as sol–gel[6], Magnetron sputtering (RF) [7], metal organic chemical vapor deposition (MOCVD) [8], and plasma-enhanced chemical vapor deposition (PECVD) [9]. However, these methods result in poor uniformity and low accuracy in film thickness control during film growth. In addition, these methods can lead to defects in high concentrations. Therefore, in some cases, the sedimentary after annealing or laser conditioning is used to improve quality [10]. Above all, compared with other deposition methods, atomic layer deposition (ALD) [11,12] demonstrates significant advantages during thin film deposition, allowing precise and convenient control of film thickness. In addition, the thin

* Corresponding author.
E-mail address: pzhyang@hotmail.com (P. Yang).

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film with uniform thickness can be fabricated on a complex substrate by using this technology.

The most important feature of this method is the self-limiting characteristic of surface chemisorption, which offers many advantages in the preparation of thin films [13]. On one hand, because of the self-limiting nature of the reaction, the thickness of the films grown in each cycle is constant as long as the amount of the precursor reaches the saturation condition. Therefore, the method has good repeatability and large area uniformity. On the other hand, the thickness of the thin film is only determined by the growth period, which can achieve accurate thickness control. Nevertheless, the material growth temperature and deposition substrate determine the surface reaction and the transformation of film structure [14]. In the HfO_2 film growth process, monoclinic polycrystalline is preferred as the main crystalline phase [15]. The substrate temperature has a significant impact on ALD thickness, polycrystalline HfO_2 film structure, and crystal size [16]. The change of the structure of the film obviously affects the optical properties of the film, which is due to that the phase affects the strain in the film and the surface roughness as well as the refractive index [17]. The increase of deposition temperature may lead to the change of crystal structure and the increase of surface roughness.

The purpose of this work was to grow HfO_2 films at variable substrate temperatures and study the effect of temperature on their structure and optical properties. The evolution from amorphous to polycrystalline phase of HfO_2 thin films can be observed at every 30 °C temperature increase during the same deposition period. The results of substrate temperature experiments show that HfO_2 thin films can play an anti-reflective role. Especially, the optimal slight fluctuation of substrate temperature causes the lowest value of anti-reflective in different bands, which provides a strong basis for new energy solar cells to absorb light energy bands. The small range fluctuation of substrate temperature affects the growth rate of the films, thus changing the refractive index of the HfO_2 films. There is also an inseparable relationship between the morphology of the films and the substrate temperature. It is well known that the microstructure of nanometer thin films is very important for optical reflectivity and refractive index. Optical parameters are affected by surface/interface structure, film roughness, crystal size, film uniformity, growth rate, deposition temperature and defect structure. Another major element, the refractive index and reflectivity characteristics play an important reference role in the practical application of optical devices. In this experimental study, HfO_2 thin films with variable microstructures were deposited at different growth temperatures (170 °C, 200 °C 230 °C, 260 °C and 290 °C) at 12 hPa. XRD was used to measure the crystallinity of HfO_2 films at different temperatures. AFM was used to characterize the roughness of the films. Spectrophotometer was used to measure the change of reflectivity. Spectral ellipsometer was used to describe the refractive index of the films. Raman was used to confirm the existence of stable monoclinic structure of HfO_2 films in polycrystalline state. In brief, this paper reported the growth temperature on the optical properties of HfO_2 film, and establish the microscopic structure and application of HfO_2 film function relation between the optical performances.

2. Experimental details

In this work, Tetra (ethyl methylamino) hafnium (TEMAHf) and deionized water (H_2O) were used as precursors to prepare HfO_2 thin films by Picosun R200 ALD system. High purity nitrogen (99.999%) was used as protective gas and carrier gas for deposition. Superfluous gas was also purged by high purity nitrogen. The thickness of p-type silicon (100) is about 0.5 mm. When cleaning the substrate, the organic substances on the surface was washed with detergent (acetone), then with deionized water in an ultrasonic washer for about 30 min, followed by ultrasonic cleaning with alcohol for 30 min, and finally washed with deionized water. Before deposition, the chamber pressure was pumped down to 12 hPa. The heating temperature of the precursor source bottle and the substrate temperature were set respectively. Then, two kinds of precursors were set up with carrier gas, pulse time and purge time parameters: hafnium precursor, the gas carrying capacity was 120 sccm. After each precursor pulse, the reaction zone was purified with nitrogen gas. The duration of the TEMAHf precursor pulse time was 1.6 s and the purification time was 5 s. The water precursor had a gas carrying capacity of 150 sccm. The duration of the precursor pulse was 0.2 s and the purification time was 5 s. In this study, the substrate temperature of HfO_2 films was 170 °C – 290 °C, and the deposition period was 600 cycles.

For the deposition of HfO_2 films with temperature as a parameter under ALD, the following methods were used to characterize the films. X-ray diffraction (XRD) measurement with Cu Kα (1.54 Å) as the incident radiation (Rigaku UltimaIV) was applied to study the phase of HfO_2 films. Atomic force microscopy (AFM) was used to characterize the surface roughness of the films, and the effect of deposition temperature on the surface morphology of the films was revealed. The ultraviolet visible spectroscopy (UV–Vis) and spectroscopy ellipsometry (SE) were carried out to obtain the optical constants of HfO_2 films. A confocal micro Raman system with a 532 nm laser was used to measure the Raman spectra of the thin films. The power used was 6 mW with 40X lens with NA = 0.75.

3. Results and discussion

3.1. Crystal structure

The XRD patterns of the HfO_2 films grown at different deposition temperatures (**T**) from 170 °C to 290 °C are shown in Fig. 1. The XRD curve of HfO_2 film grown at 170 °C does not show any well-defined characteristic diffraction peaks of the crystal structure, indicating that the film is in an amorphous structure. When the deposition temperature rises to 200 °C, the XRD pattern of the HfO_2 film starts to show some hints of discrete peaks, indicating that the film has begun to transform into a polycrystalline state, but is still mostly in an amorphous state, which may be attributed to the presence of small crystals in an amorphous matrix. When the deposition temperature is greater than 200 °C, the XRD pattern of the film begins to show characteristic peaks of the crystal structure, indicating that the film has been transformed into the polycrystalline state. In order to form a crystalline phase, deposited atoms should have enough energy, which enables the atom to be able to locate itself at a low energy position leading to the formation of the

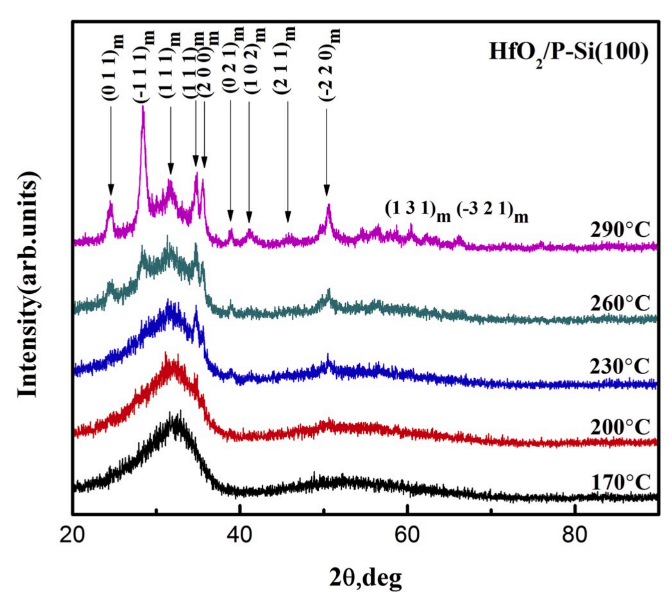

Fig. 1. XRD patterns of samples with different deposition temperatures (T).

crystalline phase. High substrate temperature can generate enough energy to produce crystalline phase. From Fig. 1, XRD characterization indicates that the HfO_2 films grown at deposition temperatures less than 200 °C are amorphous while films grown at **T** greater than or equal to 200 °C are polycrystalline and oriented [18]. The preferred orientation of crystal growth is different in different temperature ranges. In the 200–230 °C range, (200), (−220) peaks emerge first, but in the 260–290 °C range, (−111), (011) peaks grow preferentially. This indicates that the crystallization temperature of monoclinic HfO_2 (P21/C) is around 200 °C and the crystalline domain size increases with the increase of **T**. Considering the stability of the phase, the film exhibits a strong (−111) orientation, which may due to the existence of the lowest surface free energy, although there are some other small peaks, which may be due to the preferential orientation of other crystal directions at a higher temperature. The microcrystals with the (−111) plane perpendicular to the growth direction in the film represent the lowest energy direction and are thermodynamic preferred [19]. The results show that the deposition temperature plays an important role in the growth of thin film crystals.

Fig. 2 shows the Raman spectra of HfO_2 thin films grown at different temperature (170 °C, 200 °C, 230 °C, 260 °C and 290 °C) with 600 cycles. Raman spectra were obtained in the range of 130–900 cm^{-1} excited at 532 nm. The theoretical analysis of HfO_2 Raman spectrum show that 36 phonon modes exist in monoclinic structure, among them 18 (9Ag+ 9Bg), 15 (8Au+ 7Bu), and 3 are Raman active modes, IR active modes, and zero-frequency translation modes, respectively [20]. The strongest peak at ~520 cm^{-1} and 301 cm^{-1} peak Fig. 2 is from the Si substrate. Among them, the films deposited at 170 °C show very wide signals, which is attributable to the fact that it is still in an amorphous structure. With the increase of deposition temperature, phonon modes become tenser due to the addition of monoclonal phase in HfO_2 film. We can see that one new characteristic peaks (617 cm^{-1}) appear, which belong to Ag phonon modes [21]. The peak position at 301 cm^{-1} Fig. 2 locally enlarged illustration is caused by the overtones of acoustic phonons. The 301 cm^{-1} peak strength of deposited hafnium oxide films is higher than that of silicon substrates, which may be caused by high frequency vibration of Hf–Hf. In addition, the peak position of 617 cm^{-1} is caused by Hf–O or O–O high-frequency vibration [22]. However, when the substrate temperature was 290 °C, the peak position of 617 cm^{-1} became very wide, possibly due to the stable monoclonal crystal structure and weakened Hf–O or O–O vibration mode.

3.2. Film thickness and growth rate

Fig. 3 (a) shows the dependence of the film thickness on substrate temperature on p-type silicon substrates, measured by SE. It can be seen that the film thickness decreases with the increase of temperature from 170 °C to 290 °C. An approximate linear relationship between the film growth rate and substrate temperature was obtained. This phenomenon can be explained as follows: at a lower substrate temperature, the growth rate is slightly higher, which means that after each water pulse, the density of active adsorption sites is higher and hydroxyl groups are formed on the surface. With the increase of temperature, the number of OH-groups to participate in the surface reaction reduces[23]. Indeed, the deposition temperature increasing from 170 °C to 290 °C causes a reduction of growth rate by a factor of 1.4 (Fig. 3). In Fig. 3b, we can see that the films appears in different colors, blue, pink, lavender, light yellow, dark yellow, respectively, on p-type silicon substrates, reflecting the variation in the film thickness.

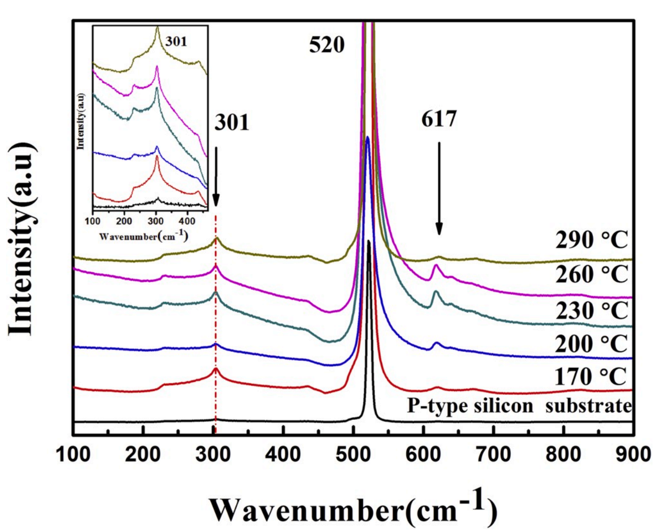

Fig. 2. Raman spectra of HfO_2 thin films of different deposition temperatures.

3.3. Optical properties

Fig. 4 (a) shows the reflectance spectra of the HfO_2 films deposited at different temperatures and silicon wafer without deposition of HfO_2 film. The reflectance spectra were measured with a UV-3600 (SHIMADZU, Japan) spectrometer in a range from 380 to 1300 nm. Compared with the silicon wafer without deposition of HfO_2 film, all ALD deposited films exhibit decreased reflectivity. All the HfO_2 films exhibit a reflectivity minimum in the visible spectral region with the wavelength of the minimum depending on the film thickness, a rapid increase in the ultraviolet region, and significant reduction from the Si reflectance in the near infrared region. The plasma wavelength is usually close to the wavelength of the reflectivity minimum [24,25]. In addition, a short plasma wavelength and high infrared reflectivity are two key factors of thermal reflector. On this regard, Fig. 4 (a) shows a weak reflectivity in the spectral range of 400 nm–600 nm, and an increased reflectivity up to about 33% in the near infrared region, indicating a moderate thermal mirror effect [26]. Therefore, in the 400 nm–600nm transparent band, due to the internal mechanism of optical loss and the external cause of optical loss, the low surface roughness (AFM test results Table 1), high purity and structural uniformity of the film make the reflection weaken and the substrate absorption strengthen. From Fig. 4 (a), we can observe another phenomenon. For each substrate temperature, the reflectance of the minimum wavelength point decreases to close to zero, and as the temperature increases, the minimum wavelength point is blue-shifted. One of the reasons for this phenomenon is the increase of the crystalline ordering and the increase of the packing density, which causes the stress concentration in the crystal lattice. Lattice contraction decreases the film thickness, which in turn leads to the reduction in structural defects and roughness with increasing substrate temperature [27]. Therefore, this study provides a method to further reduce the reflectance of HfO_2 film as AR optical coating.

Refractive index profiles of the HfO_2 films deposited at different temperatures are shown in Fig. 4 (b). The optical model of HfO_2 used in SE fitting is a Cauchy model, which is defined as follows [28]:

$$\mathbf{n}(\lambda) = \mathrm{A} + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \quad (1)$$

$$\mathrm{k} = 0 \quad (2)$$

where A, B, and C are the material coefficients that define the real part of the refractive index $\mathbf{n}(\lambda)$, and $\mathbf{k}$ is the extinction coefficient. It can be found that the refractive index of the film increases with the increase of deposition temperature. The refractive index of the film is found increasing at a given wavelength while the deposition temperature increases. As is known to all, the temperature of the process parameters has a certain effect on the refractive index of the HfO_2 Thin films grown. In general, a higher refractive index means more compact film structure is obtained. In particular, the refractive index of films deposited at 170 °C are significantly lower than that of films deposited at higher

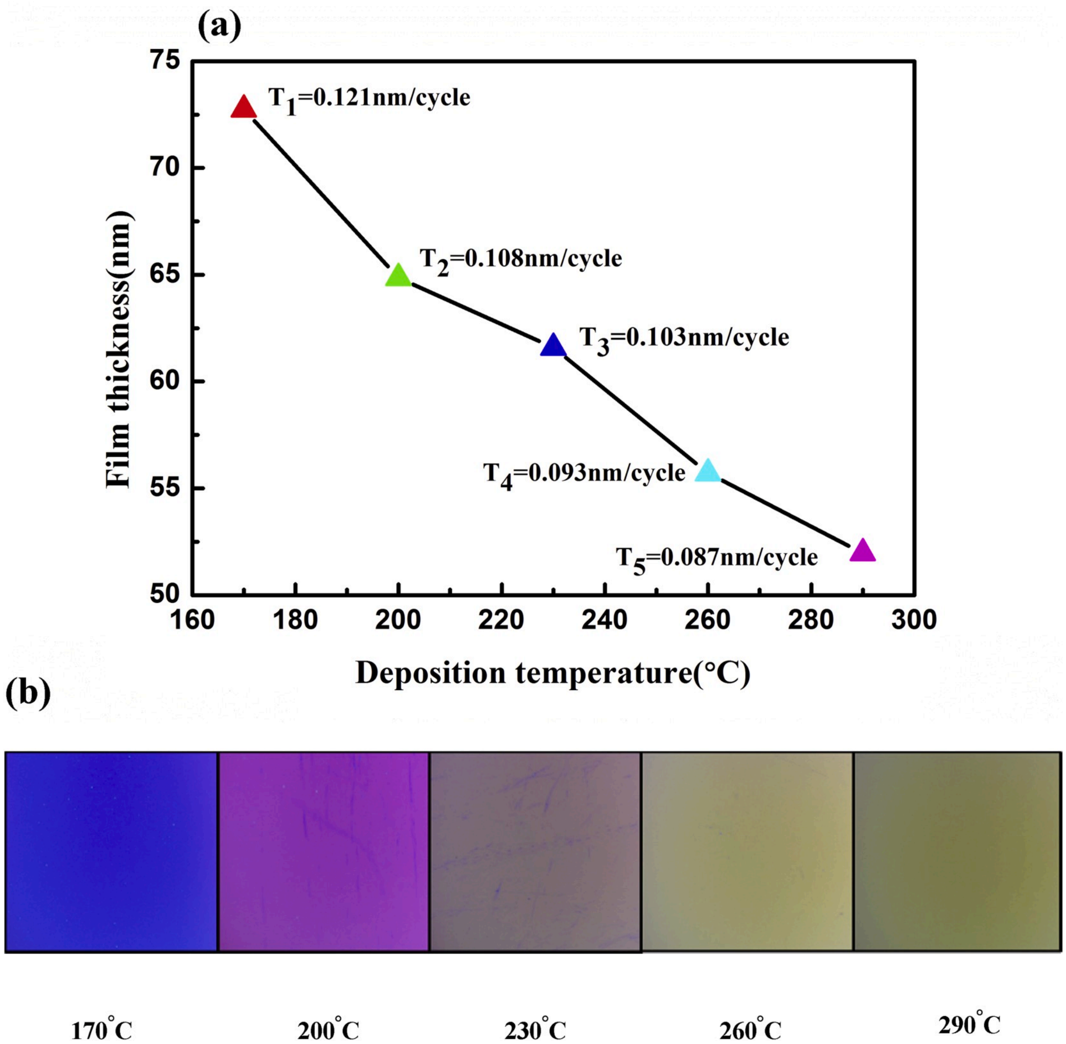

Fig. 3. (a) Relationship between film thickness and deposition temperatures. (b) Photographs showing coloring of corresponding HfO_2 layers, where the samples were illuminated by Olympus optical microscope.

temperatures. Because the structure of the films deposited at 170 °C is amorphous, and its structure compactness is poor. Microcrystals begin to appear at 200 °C, and the film structure compactness gradually becomes better. **n** increases with increasing substrate temperature, which may be due to increasing membrane density, grain size and crystallinity [29]. The inset of Fig. 4b shows that with the increase of deposition temperature, the refractive index gradually increase from 2.03 (for the film deposited at 170 °C) to 2.07 (for the film deposited at 290 °C). We use the refractive indexes at λ = 632 nm to evaluate porosity (**P**) and packing density (**PD**) at different substrate temperatures using following equations [30,31]:

$$P(\%) = \left[1 - \left(\frac{n_f^2 - 1}{n_b^2 - 1}\right)\right] \bullet 100\% \tag{3}$$

$$PD = \left(\frac{n_f^2 - 1}{n_f^2 + 2}\right)\left(\frac{n_b^2 + 2}{n_b^2 - 1}\right) \tag{4}$$

Values of refractive index $\mathbf{n_b}$ for bulk HfO_2 is equal to 2.098 at 632 nm [32]. $\mathbf{n_f}$ is the refractive index of the HfO_2 film at 632 nm. For the film of the minimum deposition temperature of 170 °C, the minimum filling density is 0.96. As the deposition temperature increases, the filling density (Fig. 4c) gradually increases to 0.973, 0.975, 0.979, 0.984, respectively. The porosity value (Fig. 4c) is inversely proportional to the filling density, and thus decreases as the deposition temperature increases: from 5.5% for 170 °C to 3.4% for 290 °C. This phenomenon is due to the enhanced attraction between Hf^{4+}-O^{2-} dipoles, lattice contraction and film density increase. It can be considered that the film with the highest deposition temperature has the most compact structure. This also indicates that ALD prepared films can have good compactness and high quality.

3.4. Surface morphology

AFM images of the films grown with various deposition temperatures with identical cycles are shown in Fig. 5, each in a 2 μm × 2 μm area. RMS roughness $\mathbf{S_q}$, average roughness $\mathbf{S_a}$, skewness and kurtosis are important parameters to obtain the microstructural properties of a thin film. Average roughness parameters can be calculated by means of the following relations [33]:

$$Sa = \frac{1}{MN}\sum_{j=1}^{N}\sum_{i=1}^{M}|Z|(x_i, y_j), \tag{5}$$

and RMS roughness parameter can be calculated using the equation [33] :

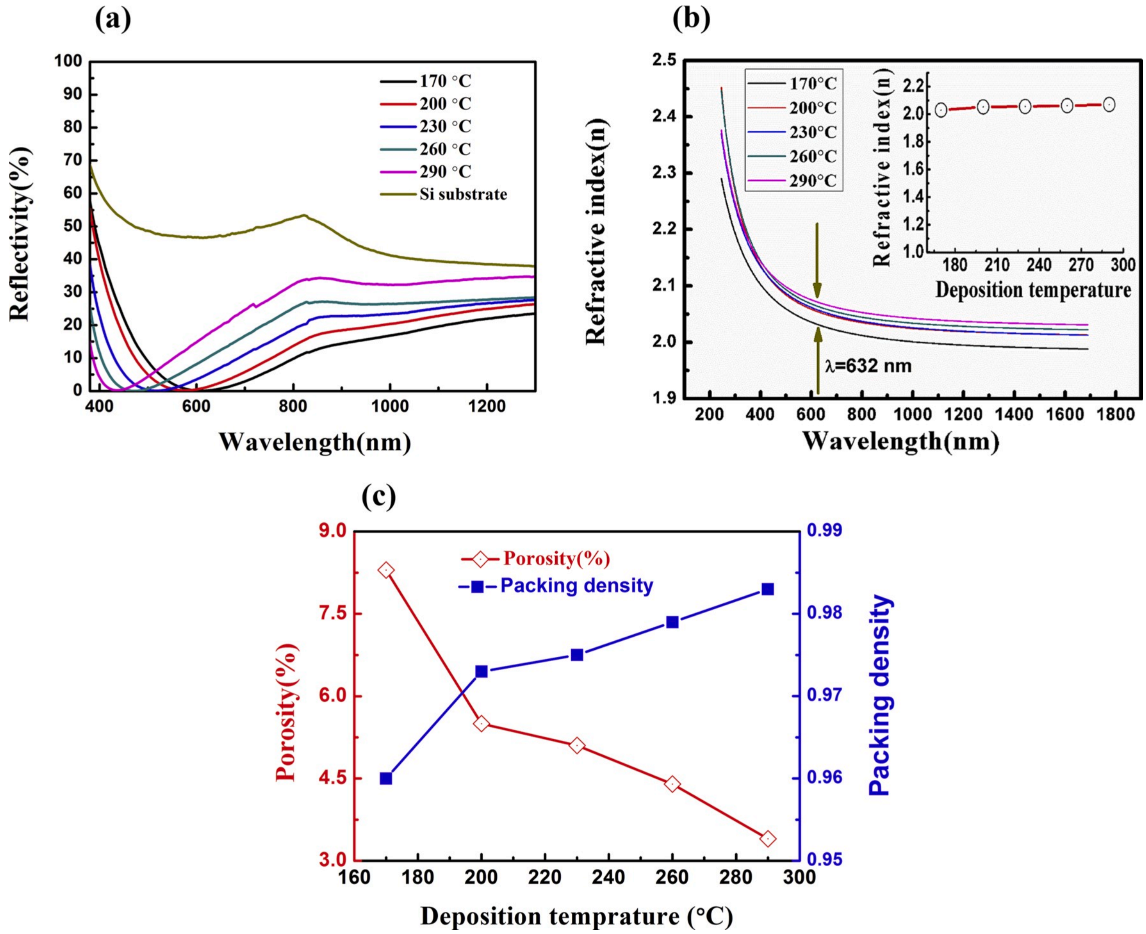

Fig. 4. (a) Reflectance spectra of HfO_2 films deposited at different substrate temperatures. (b) Wavelength dependence of refractive index for the HfO_2 films. The inset depicts the refractive index at $\lambda = 632$ nm with varying substrate temperature. (c) Packing density and porosity of the HfO_2 films deposited at different substrate temperatures.

Table 1
Surface roughness parameters of the HfO_2 thin films grown under different temperatures.

Sample	Subs. Temp. (°C)	RMS roughness (nm)	Skewness (s)	Kurtosis (k)	Average roughness (nm)
1	170 °C	1.514	−2.423	8.544	1.105
2	200 °C	2.257	−2.220	8.292	1.502
3	230 °C	2.752	−1.524	4.972	2.112
4	260 °C	3.106	−0.859	3.346	2.541
5	290 °C	2.883	0.408	2.805	2.289

$$Sq = \sqrt{\frac{1}{MN}\sum_{j=1}^{N}\sum_{i=1}^{M} Z^2(x_i, y_j)} \quad , \tag{6}$$

where **M** is the number of columns on the surface, and **N** is the number of lines on the surface.

The results are summarized in Table 1. It is found that the surface roughness of samples increase with the increase of substrate temperature between 170 °C and 260 °C. Sample **1** has the smallest surface roughness ($\mathbf{S_a}$: 1.105 nm, $\mathbf{S_q}$: 1.514 nm), while sample **4** has the highest surface roughness ($\mathbf{S_a}$: 2.541 nm, $\mathbf{S_q}$: 3.106 nm). The different surface roughness may be due to the variation of oxygen content in the samples [34]. However, the surface roughness of the 290 °C film decreases, which may be caused by the rearrangement of atoms resulted from the heating of high-temperature substrate, leading to the reduction of roughness and good uniformity of the film. The surface crystallization quality becomes higher and denser as the temperature increases. The results are in good agreement with **XRD** and **SE**. The above results indicate that the surface of HfO_2 film exhibits obvious high quality crystal morphology at the deposition temperature of 290 °C.

In addition to $\mathbf{R_a}$ and $\mathbf{R_q}$, two other parameters, kurtosis (**K**) and skewness (**S**), can be used to evaluate the surface symmetry distribution and peak value. Skewness and kurtosis are dimensionless factors representing the shape of distribution. The kurtosis can be computed from the following relation [35,36]:

$$K = \frac{1}{R_q^4 N}\sum_{j=1}^{N} Z_j^4 \tag{7}$$

$\mathbf{R_q}$ is the root mean square roughness. $\mathbf{Z_j}$ is the height distribution. The surface kurtosis (**K**) is a measurement of the sharpness of the features on a surface. For a Gaussian surface, the kurtosis value is 3. If the kurtosis value is greater than 3, it indicates that the distribution has many peaks or low valleys with relatively sharp features. If the kurtosis value is less than 3, the surface is uniform and flat [36]. Surface skewness (**S**) is When a Gaussian surface, its surface skewness is 0. The features of plateau and peak have positive skewness, while the features of low valleys and deep hole have negative skewness. The skewness can be computed from the following relation [35,36]:

$$S = \frac{1}{\mathbf{R_q^3 N}}\sum_{j=1}^{N} \mathbf{Z}_j^3 \tag{8}$$

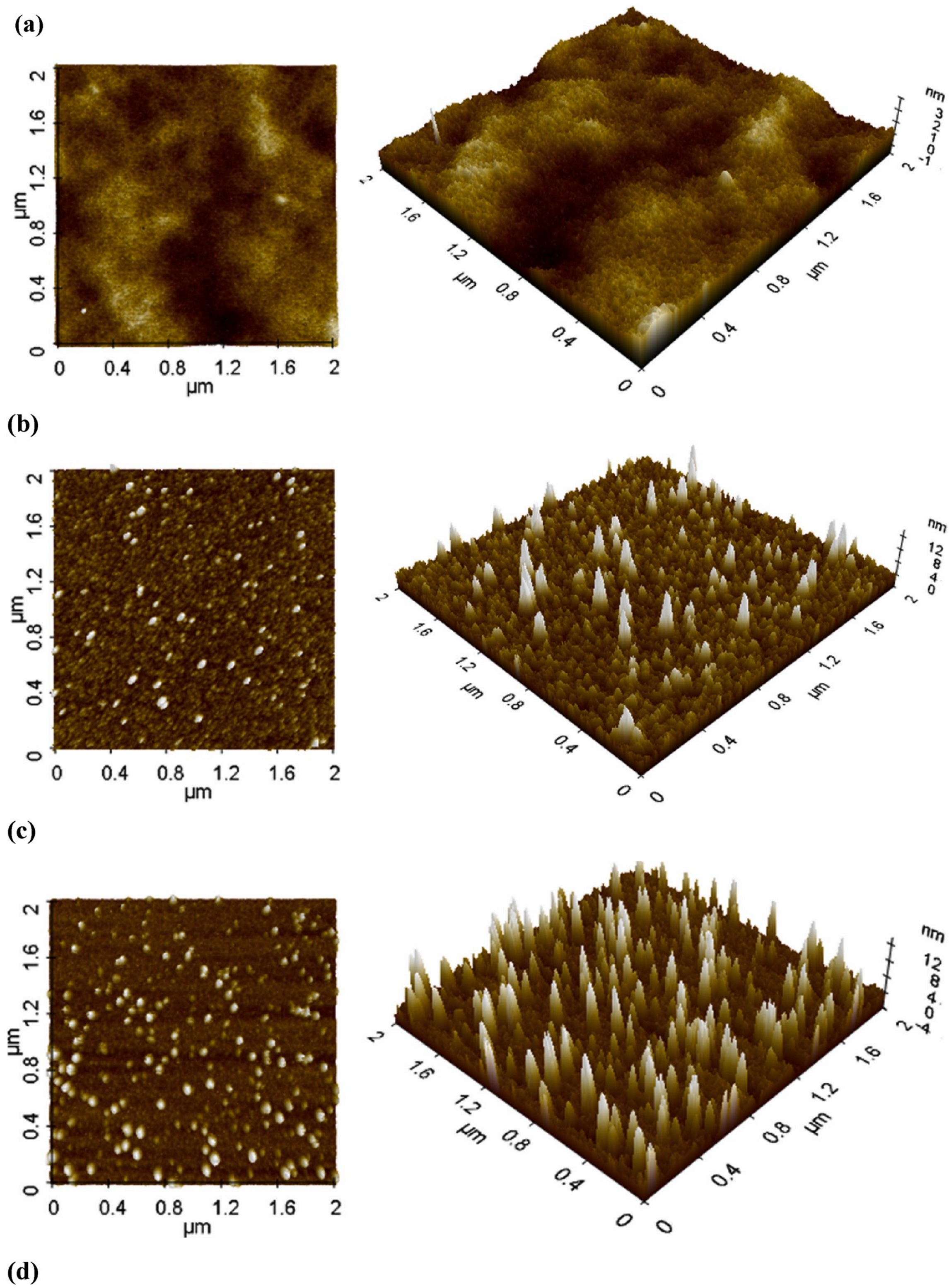

Fig. 5. AFM images of HfO_2 thin films deposited on Si (1 0 0) at (a) Si wafer, (b) 170 °C, (c) 200 °C, (d) 230 °C, (e) 260 °C, and (f) 290 °C.

The changes of kurtosis and skewness are shown in Table 1. The kurtosis values of sample 1 to sample 4 (substrate temperatures from 170 °C to 260 °C) are greater than 3, indicating that the surface height distributions are not Gaussian distribution and the surfaces have many sharp features. The kurtosis value of sample 5 is less than 3, indicating that the distribution of surface heights of sample 5 is more uniform. The skewness values are all negative for sample 1 to sample 4, but positive for sample 5 at 290 °C. The smaller values of sample 4 and sample 5 indicate that the peak and valley height distributions of them are more symmetric. In general, as the deposition temperature of the chamber increases, the kurtosis value approaches 3 and skewness value approaches 0, indicating the film surface distribution is more uniform and

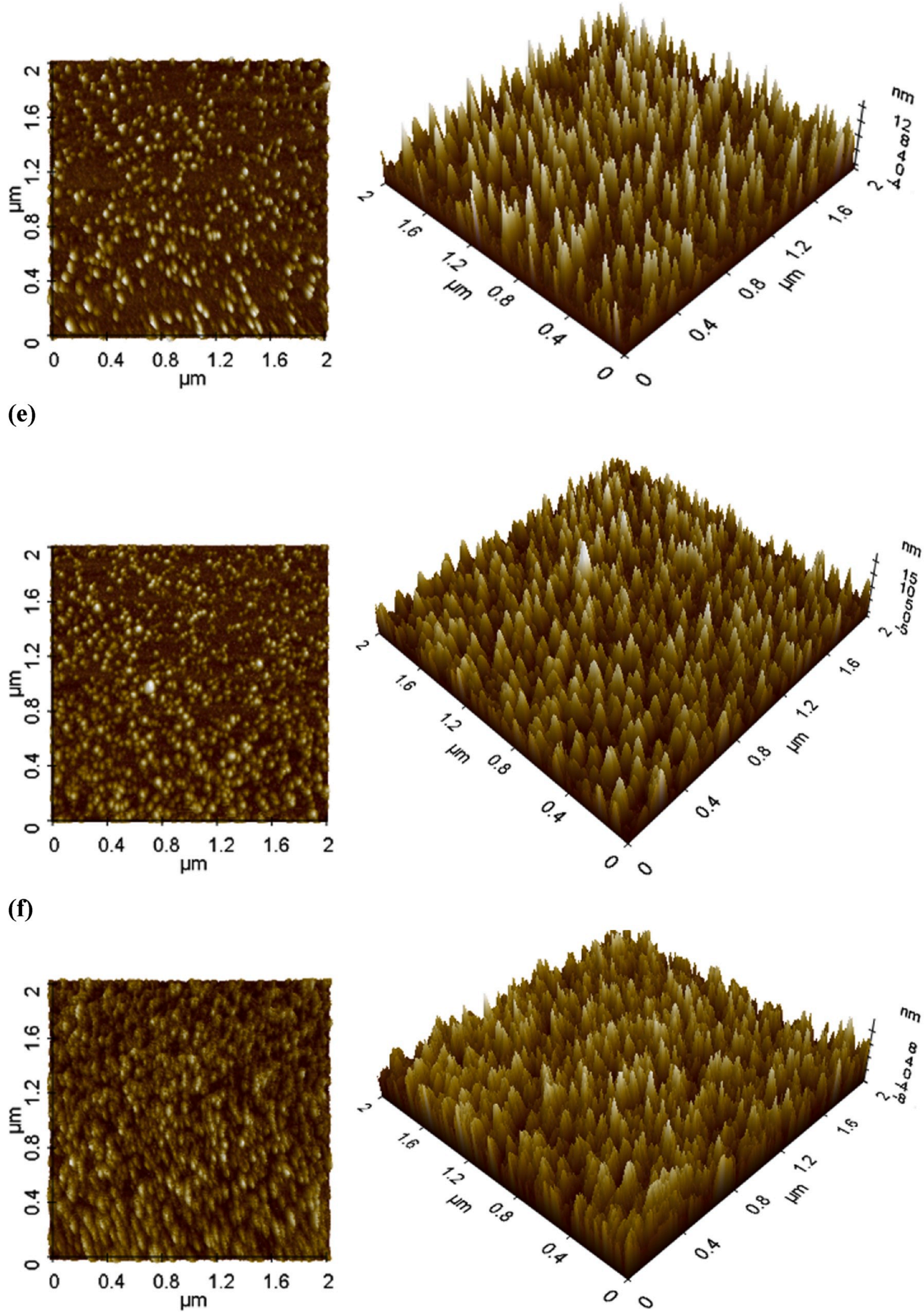

Fig. 5. (*continued*).

flat and the crystal quality has been improved.

4. Conclusion

In summary, a high-quality HfO_2 thin film has been successfully fabricated by precisely controlling the growth condition using ALD technology on the p-type silicon substrate. By carefully regulating the temperature from 170 °C to 290 °C, a gradually phase conversion from amorphous structure to polycrystalline has been observed, which is mainly attributed to the much higher energy atom induced reaction. Furthermore, the dependence of morphology and optical properties of HfO_2 films on the substrate temperature have also been systematically investigated, showing the positive effect on reducing the Fresnel reflection loss and improving the film quality under elevated temperature. More importantly, a linear relationship between film thickness and deposition temperature may provide a theoretical direction for the designed films. Considering their good anti-reflection performance and stability, the well-crystalline HfO_2 films show promising application in optoelectronic device, such as the Si solar cells to significantly enhance their solar-to-electric conversion ability.

Author contributions

Peizhi Yang. conceived the idea of the study and formulated research plan; Yong Zhang. helped to revise the paper. Wen Yang and Dewei Yang analysed the data; Xiaobo Chen, Hengli Zhao and Jing Hou. interpreted the results; Sai Li. Carried out relevant experiments and wrote the paper; all authors discussed the results and revised the manuscript.

Declaration of competing interest

This manuscript has not been published elsewhere in whole or in part. All authors have read and approved the content, and have agreed to submit it for consideration for publication in the journal. There are no conflicts of interest involved in the article.

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References

[1] J.M. Khoshman, M.E. Kordesch, Optical properties of a-HfO_2 thin films, Surf. Coating. Technol. 201 (6) (2006) 3530–3535, https://doi.org/10.1016/j.surfcoat.2006.08.074.
[2] S. Jena, R.B. Tokas, S. Tripathi, et al., Influence of oxygen partial pressure on microstructure, optical properties, residual stress and laser induced damage threshold of amorphous HfO_2 thin films, J. Alloys Compd. 771 (2019) 373–381, https://doi.org/10.1016/j.jallcom.2018.08.327.
[3] G. Abromavičius, S. Kičas, R. Buzelis, High temperature annealing effects on spectral, microstructural and laser damage resistance properties of sputtered HfO_2 and HfO_2-SiO_2 mixture-based UV mirrors, Opt. Mater. 95 (2019) 109245, https://doi.org/10.1016/j.optmat.2019.109245.
[4] Y. Wang, Z. Lin, X. Cheng, H. Xiao, F. Zhang, S. Zou, Study of HfO_2 thin films prepared by electron beam evaporation, Appl. Surf. Sci. 228 (2004) 93–99, https://doi.org/10.1016/j.apsusc.2003.12.028.
[5] E. Cianci, A. Lamperti, G. Tallarida, et al., Advanced protective coatings for reflectivity enhancement by low temperature atomic layer deposition of HfO_2 on Al surfaces for micromirror applications, Sensor Actuator Phys. 282 (2018) 124–131, https://doi.org/10.1016/j.sna.2018.09.028.
[6] M.G.S. Rao, A. Sánchez-Martinez, G. Gutiérrez-Heredia, et al., Sol-gel derived low temperature HfO_2-GPTMS hybrid gate dielectric for a-IGZO thin-film transistors (TFTs), Ceram. Int. 44 (14) (2018) 16428–16434, https://doi.org/10.1016/j.ceramint.2018.06.056.
[7] C.F. Liu, X.G. Tang, X.B. Guo, et al., Photodiode characteristics of HfO_2 thin films prepared by magnetron sputtering, Mater. Des. (2019) 108465, https://doi.org/10.1016/j.matdes.2019.108465.
[8] A. Stesmans, V.V. Afanas' ev, Defect correlated with positive charge trapping in functional HfO_2 layers on (100) Si revealed by electron spin resonance: evidence for oxygen vacancy? Microelectron. Eng. 178 (2017) 112–115, https://doi.org/10.1016/j.mee.2017.04.035.
[9] K.J. Choi, J.H. Kim, S.G. Yoon, W.C. Shin, Structural and electrical properties of HfOxNy and HfO_2 gate dielectrics in TaN gated nMOSCAP and nMOSFET devices, J. Vac. Sci. Technol. B Microelectron. Nanom. Struct. 22 (2004) 1755–1758, https://doi.org/10.1116/1.1771664.
[10] C. Wang, Y. Jin, D. Zhang, J. Shao, Z. Fan, A comparative study of the influence of different post-treatment methods on the properties of HfO_2 single layers, Optic Laser. Technol. 41 (2009) 570–573, https://doi.org/10.1016/j.optlastec.2008.10.013.
[11] J. Aarik, H. Mändar, M. Kirm, L. Pung, Optical characterization of HfO_2 thin films grown by atomic layer deposition, Thin Solid Films 466 (2004) 41–47, https://doi.org/10.1016/j.tsf.2004.01.110.
[12] J. Niinistö, M. Mäntymäki, K. Kukli, L. Costelle, E. Puukilainen, M. Ritala, M. Leskelä, Growth and phase stabilization of HfO_2 thin films by ALD using novel precursors, J. Cryst. Growth 312 (2010) 245–249, https://doi.org/10.1016/j.jcrysgro.2009.10.028.
[13] S.M. George, Atomic layer deposition: an overview, Chem. Rev. 110 (2010) 111–131, https://doi.org/10.1021/cr900056b.
[14] K. Kukli, J. Aarik, T. Uustare, J. Lu, M. Ritala, A. Aidla, L. Pung, A. Hårsta, M. Leskelä, A. Kikas, V. Sammelselg, Engineering structure and properties of hafnium oxide films by atomic layer deposition temperature, Thin Solid Films 479 (2005) 1–11, https://doi.org/10.1016/j.tsf.2004.11.191.
[15] J. Aarik, A. Aidla, A. Kikas, T. Käämbre, R. Rammula, P. Ritslaid, T. Uustare, V. Sammelselg, Effects of precursors on nucleation in atomic layer deposition of HfO_2, Appl. Surf. Sci. 230 (2004) 292–300, https://doi.org/10.1016/j.apsusc.2004.02.048.
[16] M. Ritala, M. Leskelä, L. Niinistö, T. Prohaska, G. Friedbacher, M. Grasserbauer, Development of crystallinity and morphology in hafnium dioxide thin films grown by atomic layer epitaxy, Thin Solid Films 250 (1994) 72–80, https://doi.org/10.1016/0040-6090(94)90168-6.
[17] R. Rammula, J. Aarik, H. Mändar, P. Ritslaid, V. Sammelselg, Atomic layer deposition of HfO_2 : effect of structure development on growth rate, morphology and optical properties of thin films, Appl. Surf. Sci. 257 (2010) 1043–1052, https://doi.org/10.1016/j.apsusc.2010.07.105.
[18] B. Aguirre, R.S. Vemuri, D. Zubia, M.H. Engelhard, V. Shutthananadan, K. K. Bharathi, C.V. Ramana, Growth, microstructure and electrical properties of sputter-deposited hafnium oxide (HfO_2) thin films grown using a HfO_2 ceramic target, Appl. Surf. Sci. 257 (2011) 2197–2202, https://doi.org/10.1016/j.apsusc.2010.09.072.
[19] A. Chelouche, T. Touam, M. Tazerout, D. Djouadi, F. Boudjouan, Effect of Li codoping on highly oriented sol-gel Ce-doped ZnO thin films properties, J. Lumin. 188 (2017) 331–336, https://doi.org/10.1016/j.jlumin.2017.04.047.
[20] T. Tan, Z. Liu, H. Lu, W. Liu, H. Tian, Structure and optical properties of HfO_2 thin films on silicon after rapid thermal annealing, Opt. Mater. 32 (2010) 432–435, https://doi.org/10.1016/j.optmat.2009.10.003.
[21] X. Zhao, D. Vanderbilt, Phonons and lattice dielectric properties of zirconia, Phys. Rev. B Condens. Matter 65 (2002) 1–10, https://doi.org/10.1103/PhysRevB.65.075105.
[22] A. Ramadoss, K. Krishnamoorthy, S.J. Kim, Novel synthesis of hafnium oxide nanoparticles by precipitation method and its characterization, Mater. Res. Bull. 47 (9) (2012) 2680–2684, https://doi.org/10.1016/j.materresbull.2012.05.051.
[23] J. Aarik, A. Aidla, A.A. Kiisler, T. Uustare, V. Sammelselg, Influence of substrate temperature on atomic layer growth and properties of HfO_2 thin films, Thin Solid Films 340 (1999) 110–116, https://doi.org/10.1016/S0040-6090(98)01356-X.
[24] K.L. Chopra, S. Major, D.K. Pandya, Transparent conductors—a status review, Thin Solid Films 102 (1) (1983) 1–46.
[25] E. Shanthi, V. Dutta, A. Banerjee, K.L. Chopra, Electrical and optical properties of tin oxide films doped with F and (Sb+F), Cit, J. Appl. Phys. 51 (1980) 1615, https://doi.org/10.1063/1.327610.
[26] M. Ramzan, A.M. Rana, E. Ahmed, A.S. Bhatti, M. Hafeez, A. Ali, M.Y. Nadeem, Optical description of HfO_2/Al/HfO_2 multilayer thin film devices, Curr. Appl. Phys. 14 (2014) 1854–1860, https://doi.org/10.1016/j.cap.2014.10.023.
[27] S.B. Khan, H. Wu, L. Ma, M. Hou, Z. Zhang, HfO_2 nanorod array as high-performance and high-temperature antireflective coating, Adv. Mater. Interfaces. 4 (2017) 1–9, https://doi.org/10.1002/admi.201600892.
[28] H. Fujiwara, Principles of spectroscopic ellipsometry, 2007, https://doi.org/10.1002/9780470060193.ch4.
[29] K. Venkata Subba Reddy, A. Sivasankar Reddy, P. Sreedhara Reddy, S. Uthanna, Copper nitride films deposited by dc reactive magnetron sputtering, J. Mater. Sci. Mater. Electron. 18 (2007) 1003–1008, https://doi.org/10.1007/s10854-007-9120-0.
[30] S. Kermadi, N. Agoudjil, S. Sali, L. Zougar, M. Boumaour, L. Broch, A. En Naciri, F. Placido, Microstructure and optical dispersion characterization of nanocomposite sol-gel TiO_2-SiO_2 thin films with different compositions, Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 145 (2015) 145–154, https://doi.org/10.1016/j.saa.2015.02.110.
[31] M. Subramanian, S. Vijayalakshmi, S. Venkataraj, R. Jayavel, Effect of cobalt doping on the structural and optical properties of TiO_2 films prepared by sol-gel process, Thin Solid Films 516 (2008) 3776–3782, https://doi.org/10.1016/j.tsf.2007.06.125.
[32] S.M.A. Durrani, CO-sensing properties of hafnium oxide thin films prepared by electron beam evaporation, Sensor. Actuator. B Chem. 120 (2007) 700–705, https://doi.org/10.1016/j.snb.2006.03.034.
[33] I.V. Tudose, P. Horváth, M. Suchea, S. Christoulakis, T. Kitsopoulos, G. Kiriakidis, Correlation of ZnO thin film surface properties with conductivity, Appl. Phys. Mater. Sci. Process 89 (2007) 57–61, https://doi.org/10.1007/s00339-007-4036-3.

[34] G. Yildirim, S. Bal, M. Gulen, A. Varilci, E. Budak, M. Akdogan, Substrate effect on microstructure and optical performance of sputter-deposited TiO_2 thin films, Cryst. Res. Technol. 47 (2012) 195–201, https://doi.org/10.1002/crat.201100614.
[35] J. Liu, X. Jiang, X. Huang, S. Wu, Morphological characterization of super fine pulverized coal particle. Part 2. AFM investigation of single coal particle, Fuel 89 (2010) 3884–3891, https://doi.org/10.1016/j.fuel.2010.07.001.
[36] A. Vinod, M.S. Rathore, N.S. Rao, Effects of annealing on quality and stoichiometry of HfO_2 thin films grown by RF magnetron sputtering, Vacuum 155 (2018) 339–344, https://doi.org/10.1016/j.vacuum.2018.06.037.