Journal of Siberian Federal University. Mathematics & Physics 2021, 14(2), 224–229

DOI: 10.17516/1997-1397-2021-14-2-224-229
УДК 538.958

Energy Gap Evaluation in Microcrystalline m-HfO_2 Powder

Artem O. Shilov[*]
Sergey S. Savchenko[†]
Alexander S. Vokhmintsev[‡]
Andrey V. Chukin[§]
Maksim S. Karabanalov[¶]
NANOTECH Centre, Ural Federal University
Yekaterinburg, Russian Federation
Maksim I. Vlasov
NANOTECH Centre, Ural Federal University
Yekaterinburg, Russian Federation
Institute of High-Temperature Electrochemistryof of the Ural Branch RAS
Yekaterinburg, Russian Federation
Ilya A. Weinstein[‖]
NANOTECH Centre, Ural Federal University
Yekaterinburg, Russian Federation
Institute of Metallurgy of the Ural Branch RAS
Yekaterinburg, Russian Federation

Received 10.11.2020, received in revised form 11.01.2021, accepted 20.01.2021

Abstract. In this paper optical properties of microcrystalline HfO_2 powder are investigated. X-ray diffraction and Raman spectroscopy were used to determine that the studied samples are in monoclinic phase. Based on the analysis of the diffuse reflectance spectra and applying Kubelka-Munk formalism we evaluated the indirect bandgap value $E_g = 5.34 \pm 0.05$ eV. The calculated value is in agreement with independent data for HfO_2 thin films synthesized by various methods. The paper is based on the materials of the report presented at the first Russian scientific confererence with the participation of the international community "YENISEI PHOTONICS – 2020".

Keywords: hafnium dioxide, diffuse reflectance, absorption edge

Citation: A.O. Shilov, S.S. Savchenko, A.S. Vokhmintsev, A.V. Chukin, M.S. Karabanalov, M.I. Vlasov, I.A. Weinstein, Energy Gap Evaluation in Microcrystalline m-HfO_2 Powder, J. Sib. Fed. Univ. Math. Phys., 2021, 14(2), 224–229. DOI: 10.17516/1997-1397-2021-14-2-224-229.

Introduction

Hafnium dioxide meets great interest of modern condensed matter physics as a wide-gap high-k material with superior thermal and chemical stability. Along with the other IVB metal oxides (ZrO_2, TiO_2) HfO_2 is considered to be a promising solid-state medium for creation of the

---

[*] https://orcid.org/0000-0001-8189-2431
[†] https://orcid.org/0000-0002-6256-5483
[‡] https://orcid.org/0000-0003-2529-3770
[§] https://orcid.org/0000-0001-7611-9591
[¶] https://orcid.org/0000-0001-6619-2816
[‖] i.a.weinstein@urfu.ru https://orcid.org/0000-0002-5573-7128

non-volatile memory cells because of its physical properties and favorable valence and conduction band alignments [1–5]. Due to wide energy gap and high refractive index hafnia is used as optical coatings [6]. As downscaling of field effect transistors has become difficult, HfO_2 could also be a candidate to replace SiO_2 as gate dielectric [7]. However, a deep understanding of the fundamental features in electronic structure and of the regularities in the functional characteristics formation is required to solve problems and to further develop the application principles of hafnium dioxide in opto- and nanoelectronic devices [2]. This work is devoted to the study of the structural and optical properties of nominally pure HfO_2 powder based on the sample characterization methods and analysis of diffuse reflectance spectra.

1. Experimental

In this paper the commercial hafnia powder of the HFO-1 grade (TU 48-4-201-72) was investigated. The purity of HfO_2 powder is 99.9 %, and the concentration of ZrO_2 does not exceed 0.1 %.

HfO_2 powder was characterized by AurigaCrossBeam (Carl Zeiss) scanning electron-ion microscope (SEM) with an accelerating voltage of 1 kV, coupled with an EDS device X-max 80 (Oxford Instruments) for analysis of chemical composition. The structural properties were studied by X-ray diffraction (XRD) measurements by X'Pert PRO MPD PANalytical diffractometer with CuKα radiation operating at 40 kV and 30 mA in the 2θ range from 10° to 90°, step size 0.05°.

Raman spectra were measured using Renishaw U1000 spectrometer under excitation by Cobolt Samba solid-state laser with a wavelength of 532 nm (5 mW power) and were recorded in the extended mode within the range of 50–850 cm^{-1} with spectral resolution of 1 cm^{-1}. The measurement of the diffuse reflectance spectra was performed using double beam SHIMADZU UV-2450 spectrophotometer and integrating sphere attachment ISR-2200 in range of 220–850 nm at room temperature and with barium sulfate used as the white reference plate.

2. Results

Fig.1 shows SEM-image of the investigated powder. According to the obtained images, the size of the particles is in range 1–40 μm. Analysis of the chemical composition revealed the presence of 83.8 ± 0.5 wt.% hafnium and 16.2 ± 0.5 wt.% oxygen in the sample. The obtained ratio is close to stoichiometric one. No impurities with noticeable concentration were found in the investigated powder.

XRD pattern of the HfO_2 powder is shown in Fig. 2a. The peaks correspond to m-HfO_2 – monoclinic, baddeleyite structure, group $P2_1/c$. This conclusion was confirmed by the analysis of the Raman spectrum (Fig. 2b). 17 peaks with the most intensive mode near 500 cm^{-1} is a characteristic set for m-HfO_2. In Fig. 2b the corresponding phonon modes are presented next to the peaks. It is noteworthy that the maximum near 135 cm^{-1} is the superposition of two active modes [8].

In Fig. 2c the diffuse reflectance spectrum is shown. A sharp decrease is observed for $\lambda <$ 250 nm. Also, for $\lambda = 240$ nm local maximum is present and the reflectance R > 95 % in range of $\lambda > 400$ nm.

3. Discussion

The measured diffuse reflectance spectrum was transformed into spectral dependence for optical absorption coefficient α using Kubelka-Munk function $F(R)$ (1) [5, 9]:

$$\alpha \sim F(R) = \frac{(1-R)^2}{2R}. \tag{1}$$

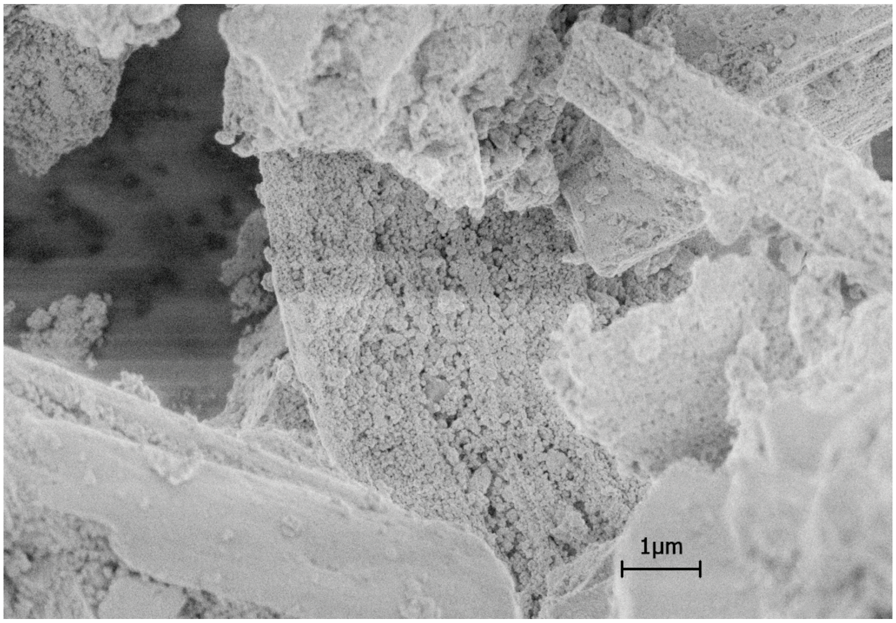

Fig. 1. SEM micrograph of HfO$_2$ powder under study

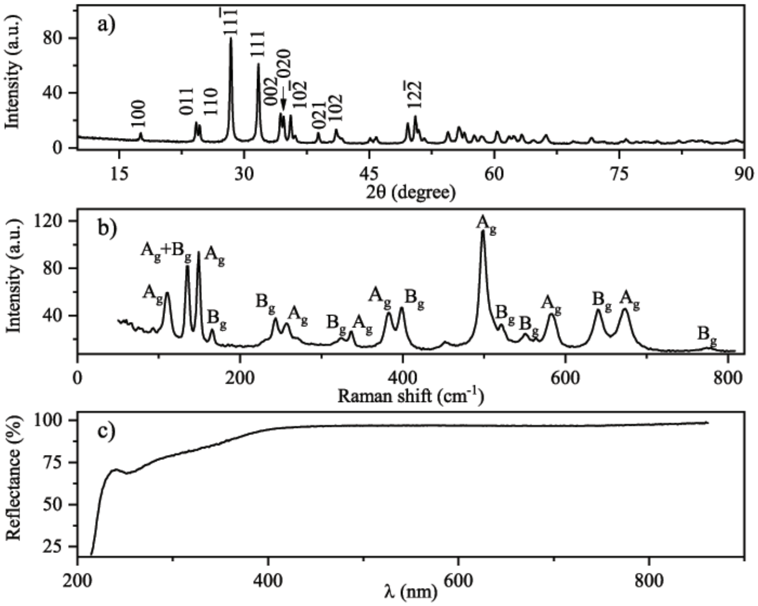

Fig. 2. Characterization of the investigated HfO$_2$ powder: a) XRD pattern, b) Raman-shift data, c) Diffuse reflectance spectrum

The obtained data is presented in Fig. 3. For the energy of incident photons $h\nu > 5.25$ eV the sharp increase due to optical transitions near intrinsic absorption edge is noted. A small broad band is observed in the energy range of 4.6–5.1 eV and an extended shoulder is present up to 3 eV. Considering the data on the absence of impurities in the studied powder we can conclude that the indicated spectral features have intrinsic origin in m-HfO$_2$ [10]. It is known that intrinsic absorption edge in m-HfO$_2$ is caused by indirect band-to-band transitions [7] and in this case should be applied (2) [11]:

$$\alpha h\nu = A(h\nu - E_g)^2, \tag{2}$$

where A is constant, $eV^{-1} \cdot cm^{-1}$.

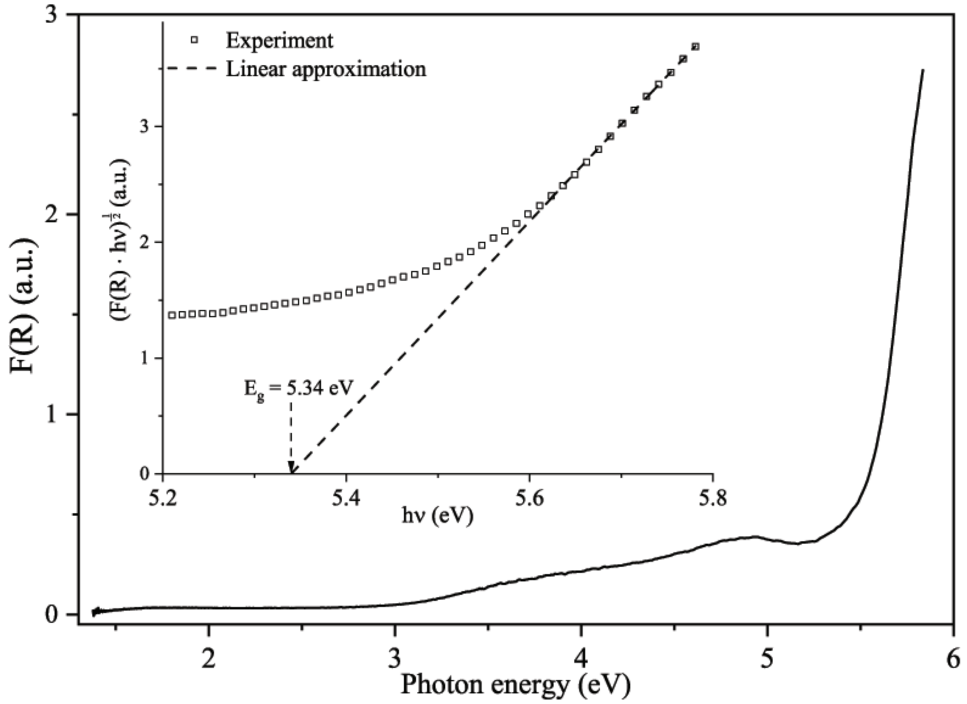

Fig. 3. Kubelka-Munk function, calculated for the diffuse reflectance spectrum. The inset shows optical bandgap evaluation

Bandgap value was evaluated using Tauc plot in coordinates $(F(R) \cdot h\nu)^{\frac{1}{2}}$. Linear part of the dependence was extrapolated in order to calculate the energy gap value E$_g$ = 5.34 ± 0.05 eV. It should be noted that this estimation was made up to emitted phonon energy $\hbar\omega$. Area of the intrinsic absorption edge $h\nu + \hbar\omega > E_g$ which corresponds to indirect transitions with absorption of vibrational modes is distorted by defect-induced processes in the band area of 4.9 eV. Nevertheless, the obtained E$_g$ value is in agreement with other independent data. In particular, for HfO$_2$ thin films of produced by ion beam sputtering deposition method E$_g$ = 5.4 ± 0.05 eV [6]. For the films synthesized using atomic-layer deposition technique energy gap value is 5.55 eV [7].

Conclusion

In this paper structural and optical properties of pure HfO$_2$ powder were studied. XRD and Raman spectroscopy methods were used to identify that the sample is stabilized in monoclinic phase. SEM was used to determine that the size of the particles is in range 1–40 μm, impurities are absent. Based on the analysis of the diffuse reflectance spectra in the region of the intrinsic absorption edge at λ <250 nm, using the Kubelka-Munk function and the Tauc plot for indirect allowed transitions, the energy gap was evaluated as E$_g$ = 5.34 ± 0.05 eV. The results obtained are consistent with independent data for thin HfO$_2$ films.

The work was supported by Act 211 Government of the Russian Federation, contract no. 02. A03.21.0006 and by Minobrnauki research project FEUZ-2020-0059.

References

[1] J.T.Gaskins,P.E.Hopkins, D.R.Merrill, S.R.Bauers, E.Hadland, D.C.Johnson, D.Koh, J.H.Yum, S.Banerjee, B.J.Nordell, M.M.Paquette, A.N.Caruso, W.A.Lanford, P.Henry, L.Ross, H.Li, L.Li, M.French, A.M.Rudolph and S.W.King, Review—Investigation and Review of the Thermal, Mechanical, Electrical, Optical, and Structural Properties of Atomic Layer Deposited High-k Dielectrics: Beryllium Oxide, Aluminum Oxide, Hafnium Oxide, and Aluminum Nitride *ECS J. Solid State Sci. Technol.* **6** (2017), 189–207.

[2] V.A.Gritsenko, D.R.Islamov, T.V.Perevalov, V.Sh.Aliev, A.P.Yelisseyev, E.E.Lomonova, V.A.Pustovarov, A.Chin, *J. Phys. Chem. C*, **120**(2016), 19980–19986.

[3] A.S.Vokhmintsev, I.A.Weinstein, R.V.Kamalov, I.B.Dorosheva, Memristive effect in a nanotubular layer of anodized titanium dioxide, *Bull. Russ. Acad. Sci. Phys.*, **78**(2014), 932–935. DOI: 10.3103/S1062873814090317

[4] I.A.Petrenyov, A.S.Vokhmintsev, R.V.Kamalov, I.A.Weinstein, Conduction mechanisms in memristors based on nanotubular arrays of zirconium oxide, AIP Conference Proceedings, Vol. 2174, 2019, 020242.

[5] A. V. Kozhevina, A. S. Vokhmintsev, R. V. Kamalov, N. A. Martemyanov, A. V. Chukin, I. A. Weinstein Optical absorption edge parameters of zirconium dioxide nanotubular structures *J. Phys.: Conf. Ser.* **917**(2017), 062031.

[6] A.O.Shilov, S.S.Savchenko, A.S.Vokhmintsev, V.A.Gritsenko, I.A.Weinstein, Optical Parameters and Energy Gap Estimation in Hafnia Thin Film, AIP Conference Proceedings, Vol. 2313, 2020. DOI: 10.1063/5.0033176

[7] J. Aarik, H. Mandar, M. Kirm, L. Pung, Optical characterization of HfO$_2$ thin films grown by atomic layer deposition *Thin Solid Films* **466**(2004), 41–47.

[8] R.Wu, B. Zhou, Q. Li, Z. Jiang, W. Wang, W. Ma, X.Zhang, Elastic and vibrational properties of monoclinic HfO$_2$ from first-principles study. *Journal of Physics D: Applied Physics* **45(12)**(2012), 125304.

[9] P. Kubelka, F. Munk,Ein Beitrag zur Optik der Farbanstriche, *Z. Tech. Phys.* **11**(1931), 593–601.

[10] E. E. Hoppe, R. S. Sorbello, C. R. Aita Near-edge optical absorption behavior of sputter deposited hafnium dioxide *J. Appl. Phys.* **101**(2007), 123534.

[11] J. Tauc, Optical Properties of Amorphous Semiconductors, *Amorphous and Liquid Semiconductors* (1974), pp.159-220.

Оценка ширины запрещенной зоны в микрокристаллическом порошке m-HfO_2

Артём О. Шилов
Сергей С. Савченко
Александр С. Вохминцев
Андрей В. Чукин
Максим С. Карабаналов
НОЦ НАНОТЕХ, Уральский федеральный университет
Екатеринбург, Российская Федерация
Максим И. Власов
НОЦ НАНОТЕХ, Уральский федеральный университет
Екатеринбург, Российская Федерация
Институт высокотемпературной электрохимии УрО РАН
Екатеринбург, Российская Федерация
Илья А. Вайнштейн
НОЦ НАНОТЕХ, Уральский федеральный университет
Екатеринбург, Российская Федерация
Институт металлургии УрО РАН
Екатеринбург, Российская Федерация

Аннотация. В работе изучены оптические свойства микрокристаллического порошка диоксида гафния. Методами рентгеновской дифракции и рамановской спектроскопии установлено, что исследуемые образцы обладают моноклинной кристаллической решёткой. На основе анализа спектров диффузного отражения и применения формализма Кубелки-Мунка выполнена оценка ширины непрямой запрещённой зоны $E_g = 5.34 \pm 0.05$ эВ. Полученная величина согласуется с независимыми данными для пленок HfO_2, синтезированных различными методами. Статья подготовлена по материалам доклада на Первой Всероссийской научной конференции с международным участием «ЕНИСЕЙСКАЯ ФОТОНИКА — 2020.»

Ключевые слова: диоксид гафния, диффузное отражение, край поглощения.