XPS and cathodoluminescence studies of HfO$_2$, Sc$_2$O$_3$ and (HfO$_2$)$_{1-x}$(Sc$_2$O$_3$)$_x$ films

Vasily V. Kaichev, Ekaterina V. Ivanova, Maria V. Zamoryanskaya, Tamara P. Smirnova, Lubov V. Yakovkina, and Vladimir A. Gritsenko

Regular Article

XPS and cathodoluminescence studies of HfO$_2$, Sc$_2$O$_3$ and (HfO$_2$)$_{1-x}$(Sc$_2$O$_3$)$_x$ films

Vasily V. Kaichev[1,a], Ekaterina V. Ivanova[2], Maria V. Zamoryanskaya[2], Tamara P. Smirnova[3],
Lubov V. Yakovkina[3], and Vladimir A. Gritsenko[4]

[1] Boreskov Institute of Catalysis, Lavrentiev ave. 5, 630090 Novosibirsk, Russian Federation

[2] Ioffe Physical Technical Institute, Polytechnicheskaya st. 26, 194021 Saint Petersburg, Russian Federation

[3] Nikolaev Institute of Inorganic Chemistry, Lavrentiev ave. 3, 630090 Novosibirsk, Russian Federation

[4] Rzhanov Institute of Semiconductor Physics, Lavrentiev ave. 13, 630090 Novosibirsk, Russian Federation

Abstract. X-ray photoelectron spectroscopy (XPS) and cathodoluminescence (CL) method have been employed to study the chemical composition and the oxygen vacancy concentration of HfO$_2$, Sc$_2$O$_3$ and (HfO$_2$)$_{1-x}$(Sc$_2$O$_3$)$_x$ films. It was found that the increase of Sc content led to monotonic decreasing the Hf4$f_{7/2}$ and Sc2$p_{3/2}$ binding energies indicating to form solid solution (HfO$_2$)$_{1-x}$(Sc$_2$O$_3$)$_x$. All the samples characterized by the intensive CL spectra with maximum around 3 eV which originated due to some radiative recombination emission caused by oxygen deficiency. The concentration of oxygen vacancy in the Sc-doped HfO$_2$ is sensitive to the Sc content and as a result the intensity of CL spectra of (HfO$_2$)$_{1-x}$(Sc$_2$O$_3$)$_x$ is lower that those of pure HfO$_2$ and Sc$_2$O$_3$.

1 Introduction

In the last years extensive research activities have focused on developing high-k dielectrics as a replacement for SiO$_2$ in complementary metal-oxide-semiconductor (CMOS) devices. Hafnium dioxide (HfO$_2$) is most frequently considered as one of the promising material because it has moderate dielectric permittivity and high thermal stability. For example, amorphous and monoclinic HfO$_2$ has permittivity of approximately 16–20, that higher by a few times then permittivity of SiO$_2$ ($\varepsilon \approx 4$). The dielectric permittivity for cubic and tetragonal HfO$_2$ achieves even 25–29 and 28–70, respectively, however both these phases exist in equilibrium only above ∼1650 °C, which is much higher than typical growth or annealing temperatures used in the CMOS processing [1,2]. At the same time, pure HfO$_2$ can suffer from a high concentration of oxygen vacancies, whose gap states lead to charge trapping shift in the transistor's gate threshold voltage [3,4]. According to calculations of Liu and Robertson [5], the doping of hafnium dioxide by group III elements such as La, Y, Sc and Al can passivate adjacent oxygen vacancies by shifting the vacancy gap state up into the conduction band. Moreover, the doping of hafnium dioxide by Sc or Dy, for example, causes growth of cubic rather than monoclinic phase that is accompanied with an increase of dielectric permittivity from 16 to 32 and a reduction of the leak-age current by up to three orders of magnitude for constant effective oxide thickness [2]. For this reasons today double oxides based on HfO$_2$ [2,6–12] attract particular attention as a possible replacement to SiO$_2$. In this work to check the influence of the Sc content in the Sc-doped HfO$_2$ on the concentration of oxygen vacancy we investigated HfO$_2$, Sc$_2$O$_3$ and (HfO$_2$)$_{1-x}$(Sc$_2$O$_3$)$_x$ films using X-ray photoelectron spectroscopy and cathodoluminescence method.

2 Experimental

All the dielectric films were grown on n-type Si(1 0 0) wafers. HfO$_2$, Sc$_2$O$_3$ and (HfO$_2$)$_{1-x}$(Sc$_2$O$_3$)$_x$ were deposited by CVD technique in a flow-type reactor using hafnium and scandium 2, 2, 6, 6-tetramethyl-3, 5-heptandionate (Hf(thd)$_4$ and Sc(thd)$_3$) as metal organic precursors in combination with molecular oxygen. The details of the process can be found elsewhere [11].

Film compositions were determined by X-ray photoelectron spectroscopy using a SPECS's machine equipped with an X-ray source XR-50 M with a twin Al/Ag anode, an ellipsoidal crystal X-ray monochromator FOCUS-500, and a hemispherical electron energy analyzer PHOIBOS-150-MCD-9. The XPS spectra were obtained using the monochromatic AlK_α radiation ($h\nu$ = 1486.74 eV) and fixed analyzer pass energy of 20 eV under ultrahigh vacuum conditions. Relative concentrations of elements were

a e-mail: vvk@catalysis.nsk.su

determined from the integral intensities of the XPS peaks using the cross-sections according to Scofield [13]. The binding energies were referenced to the C1s spectra at 284.8 eV.

Cathodoluminescence spectra were obtained in the range of 1.5–3.8 eV at room temperature using a Camebax electron beam probe microanalyzer integrated with X-ray and optic spectrometers [14]. The spectra were exited by irradiation of the samples by an electron beam with beam current of 1.2 A/cm^2 at electron energy of 5 keV when depth penetration was approximately 0.2 mkm.

3 Results and discussion

The XPS survey spectrum of HfO$_2$, Sc$_2$O$_3$ and (HfO$_2$)$_{1-x}$(Sc$_2$O$_3$)$_x$ films contains of only Hf, O, C and Sc lines (spectra not shown here). The carbon lines arise due to surface contaminations only and does not observed in the spectra after Ar$^+$-sputtering during a few minutes. Figure 1 shows the normalized Hf4f and Sc2p spectra. The Hf4f spectrum of pure HfO$_2$ is well-defined doublet according to the spin-orbital splitting into Hf4$f_{7/2}$ and Hf4$f_{5/2}$,

and the binding energies corresponding to Hf4$f_{7/2}$ and Hf4$f_{5/2}$ are 16.9 and 18.5 eV, respectively. It is in good agreement with literature where for pure HfO$_2$ the Hf4$f_{7/2}$ binding energy values in the range of 16.4–17.1 eV are cited [15–19]. Compared to the HfO$_2$, a shift of the Hf4f spectra to the lower binding energies is observed for the (HfO$_2$)$_{1-x}$(Sc$_2$O$_3$)$_x$ films suggesting that the presence of Sc modifies the Hf-O bonding characteristics.

This shift increases with Sc content. Quantitative analysis of the spectra showed that the Sc content is varied in the range of 5–30%. The results of XPS analysis are summarized in Table 1. The Sc2p spectra also consist of two lines Sc2$p_{3/2}$ and Sc2$p_{1/2}$ due to spin-orbital splitting. For pure Sc$_2$O$_3$ the Sc2$p_{3/2}$ binding energy is 401.5 eV. In the literature Sc$_2$O$_3$ is characterized by the Sc2$p_{3/2}$ binding energy in the range 401.6–402.0 eV [20–23]. For the (HfO$_2$)$_{1-x}$(Sc$_2$O$_3$)$_x$ films a shift of the Sc2$p_{3/2}$ spectra to the lower energy is also observed. It means that the structure of (HfO$_2$)$_{1-x}$(Sc$_2$O$_3$)$_x$ films conforms to a solid solution in the whole range of Sc content under study.

Characteristic cathodoluminescence spectra of monoclinic HfO$_2$, cubic Sc$_2$O$_3$ and (HfO$_2$)$_{1-x}$(Sc$_2$O$_3$)$_x$ films are shown in Figure 2. One can see that all samples
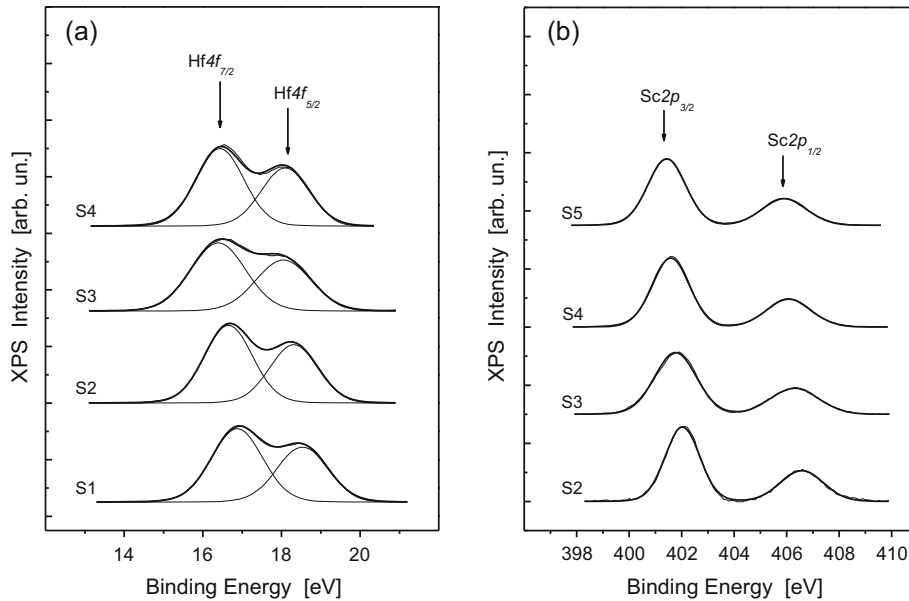
Fig. 1. The XPS Hf4f (a) and Sc2p (b) spectra of the HfO$_2$, Sc$_2$O$_3$ and (HfO$_2$)$_{1-x}$(Sc$_2$O$_3$)$_x$ films. The designation of the spectra is present in Table 1.

Table 1. The results of XPS* analysis of the HfO$_2$, Sc$_2$O$_3$ and (HfO$_2$)$_{1-x}$(Sc$_2$O$_3$)$_x$ films.

Sample	Description	Atomic ratio [Sc]/[Hf]	Binding energy, eV	
			Hf4$f_{7/2}$	Sc2$p_{3/2}$
S1	HfO$_2$	–	16.9	–
S2	(HfO$_2$)$_{1-x}$(Sc$_2$O$_3$)$_x$	0.19	16.7	402.0
S3	(HfO$_2$)$_{1-x}$(Sc$_2$O$_3$)$_x$	1.1	16.4	401.8
S4	(HfO$_2$)$_{1-x}$(Sc$_2$O$_3$)$_x$	5.2	16.4	401.6
S5	Sc$_2$O$_3$	–	–	401.5

*All XPS spectra were obtained after Ar$^+$-sputtering of the films during 3 min.
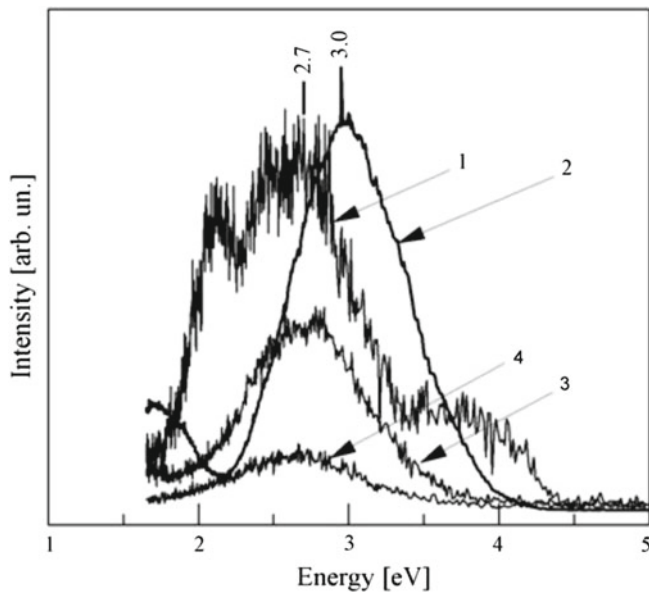
Fig. 2. Typical CL spectra: 1 – monoclinic HfO_2, 2 – cubic Sc_2O_3 (I/100), and 3, 4 – $(HfO_2)_{1-x}(Sc_2O_3)_x$ films with Sc concentration equal to 10–20 at.% respectively. All spectra were normalized on the film thickness. The intensity of Sc_2O_3 spectrum is divided by 100.

Table 2. The CL peak characteristics of the HfO_2, Sc_2O_3 and $(HfO_2)_{1-x}(Sc_2O_3)_x$ films.

Sample	Hf/Sc	Intensity, a.u.	Maximum position, eV	FWHM*, eV
HfO_2	–	140	2.7	0.85
Sc_2O_3	–	14000	3.0	0.85
$(HfO_2)_{1-x}(Sc_2O_3)_x$	9.0	70	2.7	0.85
$(HfO_2)_{1-x}(Sc_2O_3)_x$	0.4	20	2.7	0.80

*FWHM is full width at half maximum.

under study show intense cathodoluminescence in the range of 1.5–4.5 eV. The peaks at 2.1, 2.7 and 3.7 eV are observed in the spectrum of HfO_2. This is in good agreement with data by Walsh et al. [24] who studied HfO_2/Si films grown by atomic layer deposition and observed broad cathodoluminescence peaks at ∼2.0, 2.5, 3.9 and 4.3 eV. The CL spectrum of Sc_2O_3 consists of a broad peak at 3.0 eV. The intensity of Sc_2O_3 cathodoluminescence is in the two orders greater than that in the spectra of HfO_2. The $(HfO_2)_{1-x}(Sc_2O_3)_x$ film with high Sc content (20 at.%) is also characterized by cathodoluminescence peak at 2.7 eV the intensity of which is comparable with those of pure HfO_2. At the same time, the intensity of CL spectra of the $(HfO_2)_{1-x}(Sc_2O_3)_x$ film with low Sc content (10 at.%) is smaller in approximately 10 times than the intensity of CL spectra of HfO_2. The CL peak characteristics for the sample under study are listed in Table 2.

Since the energy band gap values of HfO_2 and Sc_2O_3 is approximately 5.6–6.0 eV [2,25,26] and the main intrinsic defect in the oxides is oxygen vacancy we believe that the cathodoluminescence of the samples results from

some radiative recombination emission caused by oxygen deficiency [27]. According to DFT calculations [28] there are two types of oxygen vacancies in monoclinic HfO_2: threefold- and fourfold-coordinated (V_3 and V_4, respectively) and the formation of these vacancy introduces a new double-occupied one-electron level in the band gap situated at 2.8 and 2.3 eV above the top of the valence band for V_3 and V_4. Taking into account these values, it is possible to speculate that free electron is captured into a bound state of a cation coupled with the oxygen vacancy producing the simultaneous emission of a photon with energy of approximately 3 eV. It should be noted that photoluminescence spectra of HfO_2 induced by ultraviolet photons with energy of 6–8 eV consist of a peak at 2.8 eV [29–31]. The peak at 2.1 eV in the spectrum of pure HfO_2 could be caused by issue of oxygen divacancy. This peak is not observed in the CL spectra of $(HfO_2)_{1-x}(Sc_2O_3)_x$ films. In full agreement with previous calculations of Liu and Robertson [5], the doping of HfO_2 by Sc leads to passivate of adjacent oxygen vacancies and significant decrease of the intensity of cathodoluminescence spectra (Fig. 2).

4 Conclusions

In this work we have investigated the chemical composition and the concentration of oxygen vacancy of the HfO_2, Sc_2O_3 and $(HfO_2)_{1-x}(Sc_2O_3)_x$ films using XPS and cathodoluminescence method. We showed that cathodoluminescence is a very effective method to examine the localized states presented in insulating materials like high-k dielectric films. All the samples characterize by the intensive CL spectra with maximum around 3 eV which originate due to some radiative recombination emission caused by oxygen deficiency. The concentration of oxygen vacancy in the Sc-doped HfO_2 is sensitive to the Sc content and as a result the intensity of CL spectra of $(HfO_2)_{1-x}(Sc_2O_3)_x$ is lower that those of pure HfO_2. According to the XPS data, the structure of $(HfO_2)_{1-x}(Sc_2O_3)_x$ films conforms to a solid solution in the wide range of Sc content. A monotonic increase of the energy band gap values with Sc content is observed for the films under study. Hence, our data confirm the Liu and Robertson model based on the hypothesis that group III elements (La, Sc, Y, Al) can passivate nearest-neighbor oxygen vacancies in HfO_2 by shifting the vacancy gap state up into the conduction band.

References

1. E.P. Gusev, E. Cartier, D.A. Buchanan, M. Gribelyuk, M. Copel, H. Okorn-Schmidt, C. D'Emic, Microelectron. Eng. **59**, 341 (2001)

2. C. Adelman, V. Sriramkumar, S. van Elshocht, P. Lehnen, T. Conard, S. De Gendt, Appl. Phys. Lett. **91**, 162902 (2007)

3. E. Cartier, B.P. Linder, V. Narayanan, V.K. Paruchuri, Tech. Dig. – Int. Electron Devices Meet. 57 (2006)

4. J.L. Gavartin, D.M. Ramo, A.L. Shluger, G. Bersuker, B.H. Lee, Appl. Phys. Lett. **89**, 082908 (2006)

5. D. Liu, J. Robertson, Appl. Phys. Lett. **94**, 042904 (2009)

6. H.Y. Yu, M.F. Li, B.J. Cho, C.C. Yeo, M.S. Joo, D.-L. Kwong, J.S. Pan, C.H. Ang, J.Z. Zheng, S. Ramanathan, Appl. Phys. Lett. **81**, 376 (2002)

7. V.V. Afanas'ev, A. Stesmans, W. Tsai, Appl. Phys. Lett. **82**, 245 (2003)

8. H.Y. Yu, M.F. Li, D.L. Kwong, Thin Solid Films **462-463**, 110 (2004)

9. J. Zhu, Z.G. Liu, Appl. Phys. A **80**, 1769 (2005)

10. C. Bundesmann, O. Buiu, S. Hall, M. Schubert, Appl. Phys. Lett. **91**, 121916 (2007)

11. T.P. Smirnova, M.S. Lebedev, N.B. Morozova, P.P. Semyannikov, K.V. Zherikova, V.V. Kaichev, Y.V. Dubinin, Chem. Vapor Depos. **16**, 185 (2010)

12. V.V. Kaichev, Y.V. Dubinin, T.P. Smirnova, M.S. Lebedev, J. Struct. Chem. **52**, 480 (2011)

13. J.H. Scofield, J. Electron Spectros. Relat. Phenomena **8**, 129 (1976)

14. M.V. Zamoryanskaya, S.G. Konnikov, A.N. Zamoryanskii, Instrum. Exp. Tech. **47**, 477 (2004)

15. T.P. Smirnova, V.V. Kaichev, L.V. Yakovkina, V.I. Kosyakov, S.A. Beloshapkin, F.A. Kuznetsov, M.S. Lebedev, V.A. Gritsenko, Inorganic Mater. **44**, 965 (2008)

16. T.-H. Moon, M.-H. Ham, M.-S. Kim, I. Yun, J.-M. Myoung, Appl. Surf. Sci. **240**, 105 (2005)

17. Q. Fang, J.-Y. Zhang, Z. Wang, M. Modreanu, B.J. O'Sullivan, P.K. Hurley, T.L. Leedham, D. Hywel, M.A. Audier, C. Jimenez, J.-P. Senateur, I.W. Boyd, Thin Solid Films **453–454**, 203 (2004)

18. M.-H. Cho, Y.S. Roh, C.N. Whang, K. Jeong, S.W. Nahm, D.-H. Ko, J.H. Lee, K. Fujihara, Appl. Phys. Lett. **81**, 472 (2002)

19. O. Renault, D. Samour, J.-F. Damlencourt, D. Blin, F. Martin, S. Marthon, N.T. Barrett, P. Besson, Appl. Phys. Lett. **81**, 3627 (2002)

20. K.S. Kim, N. Winograd, Chem. Phys. Lett. **31**, 312 (1975)

21. D. Grosso, P.A. Sermon, Thin Solid Films **368**, 116 (2000)

22. Y.A. Teterin, A.Y. Teterin, Russ. Chem. Rev. **71**, 347 (2002)

23. P.A.W. van der Heide, J. Electron Spectros. Relat. Phenomena **151**, 79 (2006)

24. S. Walsh, L. Fang, J.K. Schaeffer, E. Weisbrod, L.J. Brillson, Appl. Phys. Lett. **90**, 052901 (2007)

25. V.V. Afanas'ev, A. Stesmans, F. Chen, X. Shi, S.A. Campbell, Appl. Phys. Lett. **81**, 1053 (2002)

26. H. Kato, T. Nango, T. Miyagawa, T. Katagiri, K.S. Seol, Y. Ohki, J. Appl. Phys. **92**, 1106 (2002)

27. Y.-L. Chueh, L.-J. Chou, Z.L. Wang, Angew. Chem. Int. Ed. **45**, 7773 (2006)

28. A.S. Foster, F.L. Gejo, A.L. Shluger, R.M. Nieminen, Phys. Rev. B **65**, 174117 (2002)

29. T. Ito, M. Maeda, K. Nakamura, H. Kato, Y. Ohki, J. Appl. Phys. **97**, 054104 (2005)

30. T. Ito, H. Kato, Y. Ohki, J. Appl. Phys. **99**, 094106 (2006)

31. A.A. Rastorguev, V.I. Belyi, T.P. Smirnova, M.V. Zamoryanskaya, L.V. Yakovkina, V.A. Gritsenko, H. Wong, Phys. Rev. B **76**, 235315 (2007)