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The origin of 2.7 eV blue luminescence band in zirconium oxide

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The luminescence spectra of non-stoichiometric zirconium oxide film series with different oxygen vacancies' concentrations show the blue photoluminescence band centered near a 2.7 eV peak. There is a broad band at 5.2 eV in the luminescence excitation spectrum for blue emission. The *ab-initio* quantum-chemical calculation gives a peak in the optical absorption at 5.1 eV for the oxygen vacancy in cubic ZrO_2. It was concluded that the 2.7 eV blue luminescence excited near 5.2 eV in a zirconium oxide film is associated with the oxygen vacancy. © *2014 AIP Publishing LLC*.
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I. INTRODUCTION

A promising direction of the silicon microelectronics element base evolution is the application of high-κ dielectrics, such as HfO_2, ZrO_2, Ta_2O_5, etc.[1] Zirconium oxide (ZrO_2) is a prospective candidate for the role of an active medium in the next generation Resistive Random Access Memory (ReRAM).[2] The optical and transport properties of ZrO_2, as well as other high-κ dielectrics, are determined by the presence of defects in the structure. So, at present, one of the most widespread hypothesis about switching mechanism in the oxide based ReRAM consists in generating of oxygen vacancy chain that forms a conductive filament.[3,4]

An effective and informative experimental method for obtaining information about the nature of the defects in dielectrics is the luminescence analysis.[5,6] According to the literature, a blue luminescence band with an energy maximum of about 2.7 eV is observed in zirconia.[7–12] The blue luminescence is excited in the broad band near 5.2 eV.[12,13] However, the origin of the luminescence emission is unclear. Oxygen vacancies are the most probable and spread defects in oxide high-κ dielectrics.[14] Oxygen vacancies' luminescence is typical for many oxide dielectrics, such as SiO_2,[15,16] Al_2O_3,[17,18] HfO_2.[12,19,20] It has been shown that the blue luminescence of zirconia is due to intrinsic defects.[9] Thus, it leads to an assumption that oxygen vacancies are responsible for the zirconia blue luminescence band at 2.7 eV. However, previously, it has been suggested that the 2.7 eV zirconia luminescence is not related to oxygen vacancies.[12] In other studies, the origin of this peak has not yet been interpreted.

Appropriate *ab initio* calculations may clarify this problem. However, the simulation of the defects' luminescence in solids is an extremely difficult task. At the same time, it is possible to simulate the optical absorption spectra. For the most important and studied dielectrics, such as SiO_2 and Al_2O_3, the maximum of the optical absorption in the oxygen vacancy coincides with the corresponding maximum photoluminescence excitation (PLE) spectrum. Thus, the oxygen

vacancy in SiO_2 has PL band 4.4 eV and the PLE of this band with maximum at 7.6 eV.[15,16] The SiO_2 optical absorption spectrum also has its maximum at 7.6 eV.[16,21] In alumina, the oxygen vacancy related luminescence band at 3.0 eV is excited at 6.0 eV.[17,18] It has been shown that the PLE band of oxygen vacancies in Al_2O_3 coincides with the maximum optical absorption of oxygen vacancies (6.0 eV).[18,19] We believe that the same phenomenon takes place in HfO_2.[20]

There are many theoretical *ab initio* investigations of oxygen vacancies' electronic structure in ZrO_2.[22–28] Nevertheless, oxygen vacancies optical properties have not been simulated. It should be noted that optical absorption peaks at 2.8 eV and 3.3 eV have been predicted in first principle calculation of oxygen divacancy in yttrium-stabilized zirconia (YSZ).[28] At the same time, experimental peak in YSZ absorption spectra have rather wide variation from 3.3 eV to 5 eV.[29,30]

Thus, the aim of this paper is verification of our hypothesis that oxygen vacancies are responsible for the blue luminescence band at 2.7 eV and this luminescence excitation band at 5.2 eV in ZrO_2 by comparison of PLE and optical absorption spectra.

II. MATERIALS AND METHODS

For zirconia defects' luminescent properties investigations, a set of non-stoichiometric zirconium oxide films with oxygen depletion (ZrO_x, $x \leq 2$) was synthesized. The ZrO_x films were deposited on a silicon substrate by the ion beam sputtering deposition method. The substrate was placed near the zirconium target ($Zr > 99.6\%$). High-clean oxygen ($O_2 > 99.999\%$) was delivered in the substrate area while the target was bombarded by Ar^+ ions. The flow of dispersed particles from the target precipitated on the substrate surface forming a ZrO_x film. The Ar^+ ions energy was equal to 1.2 keV, whereas the density of the ion current on the Zr target was equal to 1.5 mA/cm^2. The stoichiometry of the films (value "x") was varied by the oxygen partial pressure from $(0.44–3.7) \times 10^{-3}$ Pa in the growth chamber. Unfortunately, we have not performed additional experiments to determine the stoichiometry of these films. The ZrO_x films were grown

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at room temperature. The substrate heating, due to the interaction with hot carriers from the target, did not exceed 70 °C. The ZrO$_x$ films thickness ranged from 70 to 90 nm according to the ellipsometric data. According to electron microscopy, synthesized films are amorphous.

To excite the photoluminescence (PL), a N$_2$ laser with the maximum power of 50 W/cm^2 operating at wavelength 337 nm (3.7 eV) and an Nd:YAG laser (2 W/cm^2, 263 nm, and 4.7 eV) were used. The laser beam spot on the sample was about 300 nm. At the excitation by the nitrogen laser, the spectrometer with a single diffraction monochromator equipped with the silicon CCD matrix was used to detect the PL. At the excitation by the Nd:YAG laser, we used the spectrometer with a double diffraction monochromator equipped with the cooled photomultiplier. The measurements were made at room temperature.

The PLE spectra for ZrO$_x$ films were measured at room temperature in the 200–430 nm range. A 400 W deuterium lamp LDD combined with an MDR2 diffraction monochromator was used as a light source. The light was focused on the sample, and the PL emission from the film was recorded through the color glass filters SS5+ZhS16 by an FEU 100 photomultiplier. The filters pass the light in the 440–520 nm range. The PLE spectra were corrected with the Phodamin 630 dye for the spectral distribution of quanta.

Absorption spectra simulations were performed in terms of the DFT using the Quantum-ESPRESSO software package.[31] Hybrid functional B3LYP was adopted to reproduce the accurate bandgap values. The Bloch functions of electrons in the crystal were represented by plane wave expansions with the cutoff energy of 60 Ry. The cutoff energy and grid density were selected to ensure the total cell energy convergence to within 0.005 eV/atom. The 81-atom cubic zirconia (c-ZrO$_2$) supercells were used to simulate the oxygen vacancy. The choice of the cubic phase was justified according to its simple structure and the expense of a significant amount in the required computational facilities and computation time for this kind of calculation.

III. RESULTS AND DISCUSSION

The PL spectra for ZrO$_x$ samples prepared at a different oxygen pressure, recorded at the excitation of Nd:YAG laser and N$_2$ laser, are given in Fig. 1. The PL spectra show a wide band with the average maximum at 2.7 eV, corresponding to blue emission. The peak position varies slightly (between 2.6 and 2.8 eV) depending on the samples. This effect is probably due to a different ZrO$_x$ films stoichiometry. In the PL spectra of ZrO$_x$ films prepared at the maximum oxygen pressure (1.5×10^{-3} Pa and 3.7×10^{-3} Pa), the additional narrow band with a maximum at 3.26 eV (380 nm) appeared (Fig. 1(b)). A similar PL peak of 3.17 eV was observed earlier.[13] There is no unambiguous interpretation of that peak, but it was suggested that it might be associated with the charged oxygen vacancy states.

The maximum of the PLE spectrum for the blue emission of ZrO$_x$ films prepared at a different oxygen pressure is located at 5.1–5.2 eV (Fig. 2). Since the blue PL may be excited by the 3.7 eV photons with the energy significantly lower than the
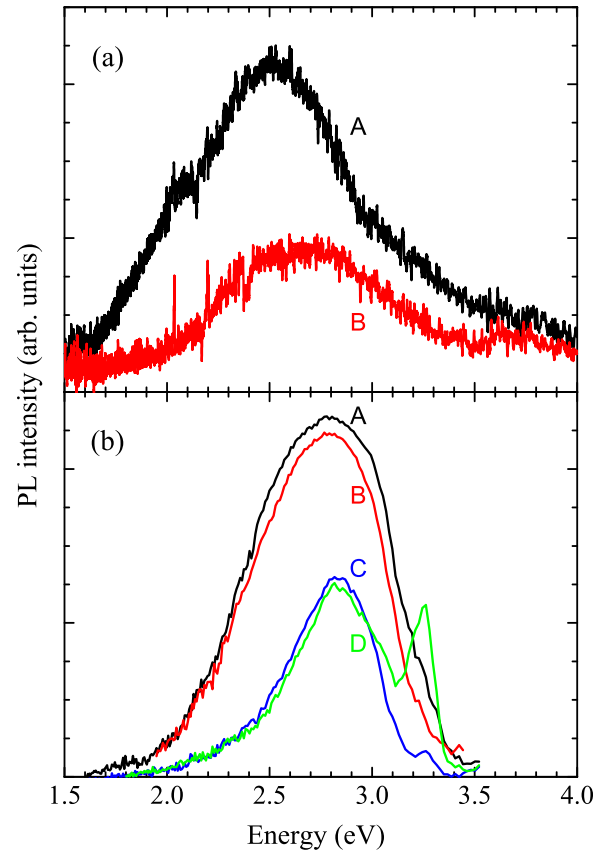

FIG. 1. The PL spectra measured at excitation by the YAG:Nd laser (a) and N$_2$ laser (b) of ZrO$_x$ films grown at different oxygen pressures: (A) 0.44×10^{-3} Pa, (B) 1.04×10^{-3} Pa, (C) 1.5×10^{-3} Pa, and (D) 3.7×10^{-3} Pa.

ZrO$_2$ bandgap (5.5–5.6 eV),[30,32] one can conclude that the blue PL is caused by radiative transitions on the defective state into the gap. The experimental PLE peaks well agree to the optical
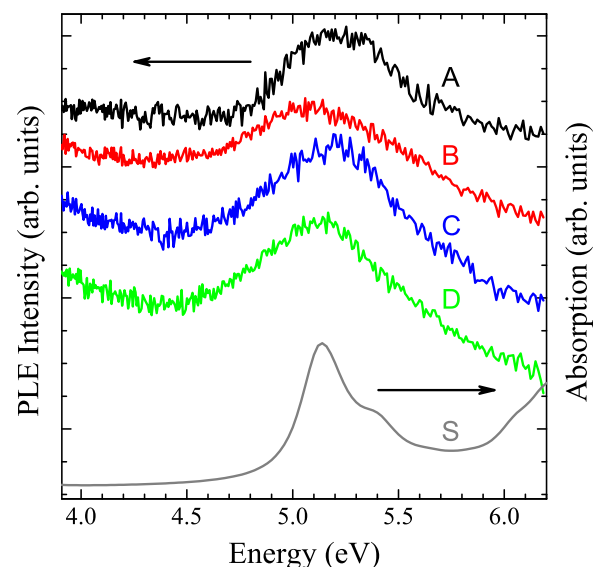

FIG. 2. Photoluminescence excitation spectra of the 2.7 eV emission band for ZrO$_x$ films grown at different oxygen pressures: (A) 0.44×10^{-3} Pa, (B) 1.04×10^{-3} Pa, (C) 1.5×10^{-3} Pa, and (D) 3.7×10^{-3} Pa. Curve (S) corresponds to simulated optical absorption spectra for the oxygen vacancy in c-ZrO$_2$. Curves are shifted on axis Y with the scale retained for convenience.

absorption maximum at 5.1 eV calculated from the first principles for the cubic phase of zirconium oxide with oxygen vacancies. The comparison of the spectra for crystalline zirconia with the experimental one for amorphous films is justified by the fact that the type of atoms and short-range order determines most of the solids physical properties. Since the excitation peak of the 2.7 eV photoluminescence band in zirconium oxide corresponds to the peak of oxygen vacancies optical absorption, we can conclude that the blue PL band of 2.7 eV is associated with oxygen vacancies.

It can be seen that the experimental PLE spectra have an appreciable intensity at energies much smaller than 5.2 eV. Previously, the similar PLE spectra behavior was observed for ZrO_2 powders of different types.[33] This phenomenon is a subject for further investigations. As shown by the theoretical simulation, there is no optical absorption in this energy range. Generally speaking, optical absorption is of different physics than the excitation of luminescence and we only know that the coinciding maxima of these spectra are caused by oxygen vacancies.

The calculation also shows the presence of absorption maxima at 5.4 eV. Interesting to note that the experimental optical absorption spectrum of the yttrium stabilized cubic zirconia has a peak absorption at energies near 5 eV.[30] At the same time, the spectrum of zirconia films' optical absorption shows a peak at 5.4 eV.[34]

As can be seen in Fig. 1, a decrease of the oxygen pressure, at which the ZrO_x films are grown, leads to an increase in the intensity of the 2.7 eV PL band. At the same time, with a decrease of the oxygen pressure in the growth chamber, the zirconia composition is becoming closer to the stoichiometric and the films' oxygen vacancy concentration increases. Thus, the blue PL band at 2.7 eV in the zirconia is caused by oxygen depletion.

A configurational diagram of the optical transitions in the neutral oxygen vacancy of ZrO_2 is shown in Fig. 3. The ground and excited states of the defect are shown. The transition with energy 5.2 eV corresponds to the optical electron excitation from the equilibrium ground state to the excited one. The relaxation from the excited state to the ground one corresponds to the radiative transition with energy 2.7 eV. This knowledge, as well as the empirical rule that thermal energy W_t is equal to half of the Stokes trap shift in the

luminescence, allows us to estimate W_t on the oxygen vacancies in ZrO_2. So, the thermal trap energy in ZrO_2 is equal to $W_t = (5.2-2.7)/2 = 1.25$ eV (Fig. 3). This information is important because the charge transfer in ZrO_2 is realized by traps.[35] Value 1.25 eV, consistent with the trap thermal energy value of 1.15 eV, was obtained in experiments in the electron transport of ZrO_2.[35] Furthermore, it is close to the theoretical value of 1.23 eV that was obtained from the quantum-chemical calculation for the negatively charged oxygen vacancy in zirconia.[27] This result gives one more validation of the findings in the present paper. Moreover, our results confirm that oxygen vacancies are electron traps and they are responsible for the charge trapping and conductivity in ZrO_2 as well as in HfO_2.[36]

IV. CONCLUSIONS

To sum it up, in this paper, a comparison of the 2.7 eV blue luminescence PLE spectra of non-stoichiometric zirconia with the calculated oxygen vacancies optical absorption in crystalline ZrO_2 has allowed us to indirectly identify the defect responsible for the blue luminescence of ZrO_2. It is shown that the blue PL with energy 2.7 eV and the corresponding excitation band 5.2 eV of zirconium oxide are due to optical transitions in the oxygen vacancies. The blue luminescence band of 2.7 eV increases with the increasing degree of oxygen depletion (i.e., due to the increase in the oxygen vacancies concentration). The obtained value for trap thermal energy 1.25 eV in ZrO_2, consistent with theoretical trap thermal energy value 1.23 eV, was received for the negatively charged oxygen vacancy in zirconia.
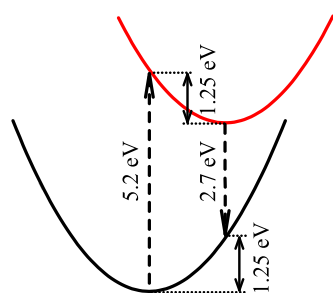
FIG. 3. Configuration energy diagrams of optical transition on the neutral oxygen vacancy in zirconia. The lower term corresponds to an occupied state of the defect, and the upper term corresponds to an unfilled excited state. The arrows indicate optical transitions during excitation (5.2 eV) and luminescence (2.7 eV).

[1]J. Robertson, Rep. Prog. Phys. **69**, 327 (2006).
[2]H. Zhang, B. Gao, B. Sun, G. Chen, L. Zeng, L. Liu, X. Liu, J. Lu, R. Han, J. Kang, and B. Yu, Appl. Phys. Lett. **96**, 123502 (2010).
[3]J. Borghetti, G. S. Snider, P. J. Kuekes, J. J. Yang, D. R. Stewart, and R. S. Williams, Nature **464**, 873 (2010).
[4]M.-J. Lee, C. B. Lee, D. Lee, S. R. Lee, M. Chang, J. H. Hur, Y.-B. Kim, C.-J. Kim, D. H. Seo, S. Seo, U.-I. Chung, I.-K. Yoo, and K. Kim, Nat. Mater. **10**, 625 (2011).
[5]R. Tohmon, Y. Shimogaichi, H. Mizuno, Y. Ohki, K. Nagasawa, and Y. Hama, Phys. Rev. Lett. **62**, 1388 (1989).
[6]H. Hosono, H. Kawazoe, and N. Matsunami, Phys. Rev. Lett. **80**, 317 (1998).
[7]M. V. Zamoryanskaya and B. E. Burakov, Inorg. Mater. **36**, 844 (2000).
[8]H. K. Yueh and B. Cox, J. Nucl. Mater. **323**, 57 (2003).
[9]M. Kirm, J. Aarik, M. Jurgens, and I. Sildos, Nucl. Instrum. Methods Phys. Res. A **537**, 251 (2005).
[10]K. Smits, L. Grigorjeva, D. Millers, A. Sarakovskis, J. Grabis, and W. Lojkowski, J. Lumin. **131**, 2058 (2011).
[11]Z. Wang, J. Zhang, G. Zheng, Y. Liu, and Y. Zhao, J. Lumin. **132**, 2817 (2012).
[12]T. Ito, M. Maeda, K. Nakamura, H. Kato, and Y. Ohki, J. Appl. Phys. **97**, 054104 (2005).
[13]K. Joy, I. J. Berlin, P. B. Nair, J. S. Lakshmi, G. P. Daniel, and P. V. Thomas, J. Phys. Chem. Solids **72**, 673 (2011).
[14]M. V. Ganduglia-Pirovano, A. Hofmann, and J. Sauer, Surf. Sci. Rep. **62**, 219 (2007).

[15]C. V. Gee and M. Kastner, Phys. Rev. Lett. **42**, 1765 (1979).

[16]V. A. Gritsenko and H. Wong, Crit. Rev. Solid State Mater. Sci. **36**, 129 (2011).

[17]K. H. Lee and J. H. Crafword, Jr., Phys. Rev. B **19**, 3217 (1979).

[18]T. V. Perevalov, O. E. Tereshenko, V. A. Gritsenko, V. A. Pustovarov, A. P. Yelisseyev, C. Park, J. H. Han, and C. Lee, J. Appl. Phys. **108**, 013501 (2010).

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

[20]T. V. Perevalov, V. Sh. Aliev, V. A. Gritsenko, A. A. Saraev, V. V. Kaichev, E. V. Ivanova, and M. V. Zamoryanskaya, Appl. Phys. Lett. **104**, 071904 (2014).

[21]H. Hosono, Y. Abe, H. Imagawa, H. Imai, and K. Arai, Phys. Rev. B **44**, 12043 (1991).

[22]A. S. Foster, V. B. Sulimov, F. Lopez Gejo, A. L. Shluger, and R. M. Nieminen, Phys. Rev. B **64**, 224108 (2001).

[23]J. Robertson, K. Xiong, and B. Falabretti, IEEE Trans. Dev. Mater. Reliab. **5**, 84 (2005).

[24]J. X. Zheng, G. Ceder, T. Maxisch, W. K. Chim, and W. K. Choi, Phys. Rev. B **75**, 104112 (2007).

[25]P. J. Shen, S. P. Jiang, K. P. Ong, W. Z. Ding, P.-L. Mao, X. G. Lu, C. H. Li, and P. Wu, J. Alloys Compd. **506**, 898 (2010).

[26]C. Arhammar, C. Moyses Araujo, and R. Ahuja, Phys. Rev. B **80**, 115208 (2009).

[27]J.-H. Hur, S. Park, and U.-I. Chung, J. Appl. Phys. **112**, 113719 (2012).

[28]D. M. Ramo and A. L. Shluger, J. Phys.: Conf. Ser. **117**, 012022 (2008).

[29]V. M. Orera, R. I. Merino, Y. Chen, R. Cases, and P. J. Alonso, Phys. Rev. B **42**, 9782 (1990).

[30]I. Kosacki, V. Petrovsky, and H. U. Anderson, Appl. Phys. Lett. **74**, 341 (1999).

[31]P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo *et al.*, J. Phys.: Condens. Matter **21**, 395502 (2009).

[32]V. V. Afanas'ev and A. Stesmans, J. Appl. Phys. **102**, 081301 (2007).

[33]K. Smits, Ph.D. dissertation (University of Latvia, Riga, 2010).

[34]J. Aarik, H. Mandar, and M. Kirm, Proc. Est. Acad. Sci., Phys., Math. **52**, 289 (2003).

[35]G. Jegert, A. Kersch, W. Weinreich, U. Schröder, and P. Lugli, Appl. Phys. Lett. **96**, 062113 (2010).

[36]D. R. Islamov, V. A. Gritsenko, C. H. Cheng, and A. Chin, Appl. Phys. Lett. **105**, 222901 (2014).