Optics and Spectroscopy, 2022, Vol. 130, No. 12

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Cathodoluminescence of intrinsic defects in films La : HfZrO

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Received October 24, 2022
Revised October 24, 2022
Accepted November 01, 2022

Lanthanum-doped (La:(HfZr)O_2) nanometer films of a solid solution of hafnium oxide and zirconium oxide are of great interest for the development of a universal memory that combines an unlimited number of RAM reprogramming cycles and nonvolatile flash memory. This work is devoted to studying the cathodoluminescent properties of La : HfZrO thin films with different contents of lanthanum. It is shown that the cathodoluminescence spectra are dominated by two emission bands with intensity maxima at 2.7 and 2.2 eV. The blue band with an energy of 2.7 eV is due to an oxygen vacancy in La : HfZrO. The study of the influence of the lanthanum impurity and annealing of the samples in argon suggests that the yellow band with the emission maximum at 2.2 eV is related to the oxygen divacancy.

Keywords: luminescence, hafnium oxide, zirconium oxide, oxygen vacancy.

DOI: 10.21883/EOS.2022.12.55242.4244-22

Introduction

At present, $Hf_{0.5}Zr_{0.5}O_2$ thin films are considered as a promising element of zeropower ferroelectric random-access memory (FeRAM) with high information capacity [1–3]. The advantages of FeRAM based on $Hf_{0.5}Zr_{0.5}O_2$ are high speed, compatibility with modern CMOS technology and potentially high gigabit capacity. Unsolved mass production problems for the introducing such FeRAM are an insufficient memory window, as well as a small number of reprogramming cycles (durability), after which the ferroelectric effect disappears. A possible way to solve these problems is to dope $Hf_{0.5}Zr_{0.5}O_2$ with various metals, among which one of the most promising is Lanthanum. The use of La as a dopant leads to a significant increase in the value of the remanent polarization [3,4] FeRAM structures based on $Hf_{0.5}Zr_{0.5}O_2$ (hereinafter referred to as La:$Hf_{0.5}Zr_{0.5}O_2$) doped with 1 mol.% La exhibit about 4×10^{10} switching cycles [3].

One of the key factors determining the ferroelectric properties are the properties of charge carrier trapping centers and their concentration in the active layer [5]. It was found that as a result of repeated switching of the FeRAM structure, the memory window decreases, and the leakage currents increase due to the formation of new defects, which act as trapping centers [6]. Despite the fact that degradation determines the wear resistance of FeRAM, a systematic study of defects and trapping centers in La:$Hf_{0.5}Zr_{0.5}O_2$ has not been previously carried out. Solving this problem is important for optimizing the operation of FeRAM based on La : $Hf_{0.5}Zr_{0.5}O_2$ and predicting reliability. Due to the fact that La : $Hf_{0.5}Zr_{0.5}O_2$ is a wide gap material, the cathodoluminescence (CL) method was used to study the luminescent properties . CL is an informative method for studying defects in dielectrics [7,8]. The purpose of present work is to study the effect of defects in La : $Hf_{0.5}Zr_{0.5}O_2$ on the luminescent properties of the films.

Samples and study methods

La : $Hf_{0.5}Zr_{0.5}O_2$ films 20 nm thick were synthesized on *p*-type silicon substrates with resistance 10 $\Omega\times$cm, (100) orientations by atomic layer deposition (ALD). As precursors, one used Tetrakis [Ethylmethylamino] Hafnium ($Hf[N(C_2H_5)CH_3]_4$) and tris (Isopropylcyclopentadienyl) Lanthanum ($La\text{-}(iPrCp)_3$). Atomic layer deposition was performed in Oxford Instruments OPAL unit. Three samples were studied: an undoped sample and samples with a lanthanum content of 2.02 and 3.47 mol.%. To increase the concentration of oxygen vacancies, the Si/La : HfZrO structures were additionally annealed in argon at 800°C for an hour.

The CL spectra were obtained on a CAMEBAX electron probe micro-analyzer (Cameca, France) equipped with original designed optical spectrometer [9] at electron energy of 2.5 keV, at electron beam current of 48 nA, and at electron beam diameter of 10 μm at room temperature. The spectra were recorded in several random regions of the sample, then the CL spectra were averaged and the background was subtracted.

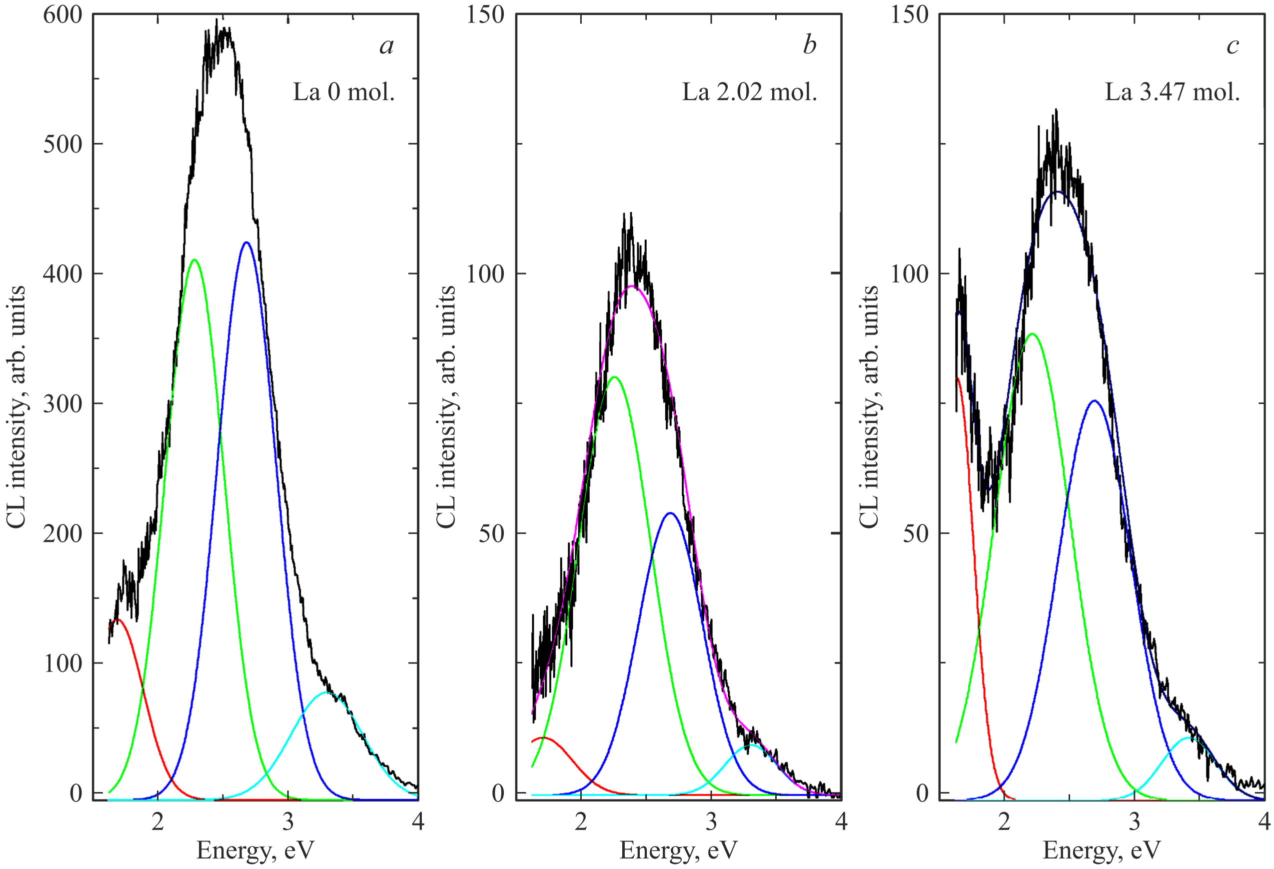

Figure 1. Cathodoluminescence spectra of La:$Hf_{0.5}Zr_{0.5}O_2$: (*a*) samples of undoped HfZrO, (*b*) La:$Hf_{0.5}Zr_{0.5}O_2$ (La 2.02 mol), (*c*) La:$Hf_{0.5}Zr_{0.5}O_2$ (La 3.47 mol). Approximation by the sum of Gaussian bands: band 1.7 eV is red line, band 2.2 eV is green line, 2.7 eV is blue line, 3.4 eV is UV line .

Experimental results and discussion

The CL spectra of the initial La:HfZrO samples are shown in Fig. 1. In the CL spectrum of the undoped sample, a broad luminescence band is observed in the visible region of the spectrum with emission maximum of 2.5 eV. According to the literature data [5,8], this band is the sum of two bands with emission maximums of 2.2 (YB) and 2.7 eV (BB). The CL spectrum also exhibits a low-energy shoulder in the infrared region of the spectrum with an energy of 1.7 eV and a high-energy shoulder in the ultraviolet region of the spectrum with an energy of 3.3 eV. Fig. 1, *a* shows the result of CL spectrum approximation by four Gaussian bands; the approximation was performed using the ORIGIN software package.

The CL spectra of samples doped with Lanthanum (Fig. 1, *b, c*) show a red shift of the maximum emission by 0.1 eV. The emission maximum for these samples is observed at 2.4 eV. This shift of the emission maximum can be explained by a change in the intensity ratio of the bands with emission maxima of 2.2 and 2.7 eV. Doping with lanthanum is also accompanied by a decrease in the total luminescence intensity compared to the luminescence intensity of the undoped $Hf_{0.5}Zr_{0.5}O_2$ sample.

At present, there is no unambiguous interpretation for the nature of the luminescence bands in the infrared region of the spectrum (1.7 eV) and in the ultraviolet region of the spectrum (3.4 eV) in the literature. A band with an emission energy of 2.7 eV (BB) was previously observed in hafnium oxide HfO_2 [1,10], in zirconium oxide ZrO_2 [11–13], in hafnium-zirconium oxide HfZrO [3]. Based on experimental data on the luminescence of these materials, electrophysical studies, photoelectron spectroscopy and quantum chemical modeling, it was found that for sky-blue luminescence band in HfO_2, ZrO_2, HfZrO are answerable the single oxygen vacancies [3,6–12]. This is confirmed in the present experiment by increase in the intensity of the 2.7 eV band after annealing the samples in an inert argon medium (Figs. 2 and 3). As can be seen from Figs 2 and 3, annealing in an inert medium also leads to an increase in the intensity of the emission band with maximum of 2.2 eV. According to the literature data, the nature of this band has no unambiguous interpretation; however, its increase in intensity after annealing suggests that it is also related to oxygen vacancies. This conclusion is also confirmed by the fact that when HfZrO is doped with an isovalent lanthanum impurity, the relative intensity of this band increases compared to the 2.7 eV band (Fig. 1), which

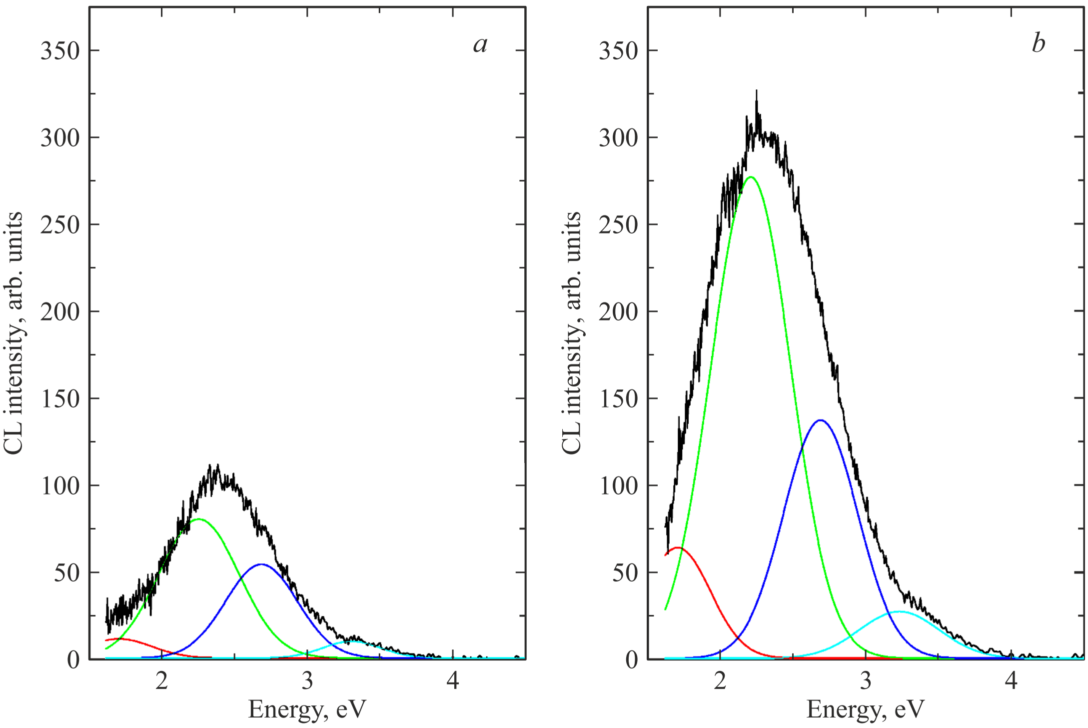

Figure 2. Cathodoluminescence spectra of doped La : $Hf_{0.5}Zr_{0.5}O_2$ (La 2.02 mol): (*a*) initial and (*b*) annealed in argon at a temperature of 800°C for 1 h. Approximation by the sum of Gaussian bands: band 1.7 eV — red line, band 2.2 eV — green line, 2.7 eV — blue line, 3.4 eV — UV line.

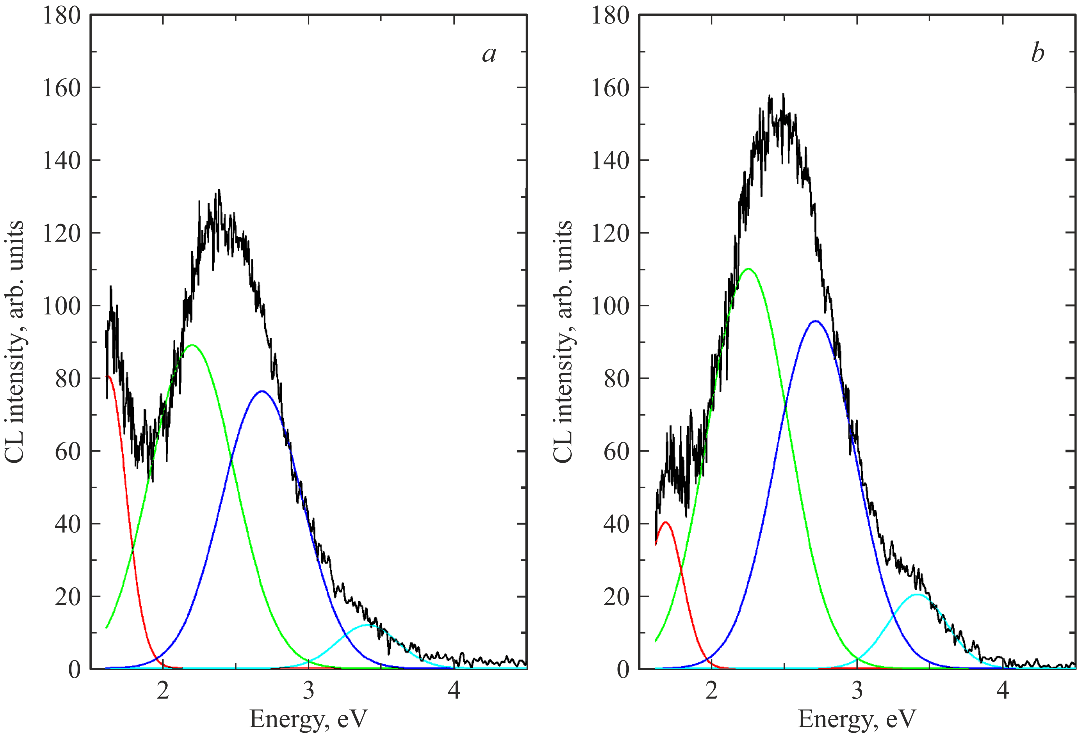

Figure 3. Cathodoluminescence spectra of doped La : $Hf_{0.5}Zr_{0.5}O_2$ (La 3.47 mol): (*a*) initial and (*b*) annealed in Argon at a temperature of 800°C for 1 h. Approximation by the sum of Gaussian bands: band 1.7 eV — red line, band 2.2 eV — green line, 2.7 eV — blue line, 3.4 eV — UV line.

leads to a red shift in the luminescence of the doped samples. This result is in favor of the fact that the band with the emission maximum at 2.2 eV is associated with the formation of oxygen polyvacancies, presumably divacancies.

Conclusion

Studies of the CL spectra of annealed and unannealed La:$Hf_{0.5}Zr_{0.5}O_2$ samples confirmed that of blue luminescence band with energy of 2.7 eV the oxygen vacancy answerable is. The change in the relative intensity of the band with an emission maximum of 2.2 eV upon doping with lanthanum, as well as the annealing of the samples in an inert medium, suggest that the CL band with a luminescence maximum of 2.2 eV (YB) is associated with oxygen divacancy.

Acknowledgments

The authors would like to thank U. Schroeder for providing the samples.

Funding

The study was supported by the RFBR grant № 20-57-12003.

Conflict of interest

The authors declare that they have no conflict of interest.

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