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Optical properties of thin erbium oxide films formed by rapid thermal annealing on SiC substrates with different structures

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Abstract. The comparative analysis of optical characteristics inherent to Er_2O_3/SiC and Er_2O_3/por-SiC/SiC structures has been performed. It has been shown that, regardless the substrate on which the Er_2O_3 film is formed, an increase in the rapid thermal annealing time leads to an improvement in the oxide film composition, with the composition of the Er_2O_3 film approaching to the stoichiometric one. At the same time, introduction of an additional porous SiC layer leads to a blurring of the oxide film/substrate interface and broadening the photoluminescence band measured in this structure.

Keywords: thin erbium oxide films, rapid thermal annealing, SiC substrates, interface, porous layer.

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1. Introduction

Despite a large number of works, the properties of oxide films of rare earth elements (REE) and MIS structures obtained on their basis have not been fully studied to date. In particular, questions related with the elucidation of the mechanisms of processes occurring on the surface and in the space charge region of semiconductor, with the search for and development of new dielectric-semiconductor systems are still unresolved [1-3].

Recently, oxides of rare-earth elements were often considered in the literature as alternative oxides used in oxide/silicon structures [4-11]. These oxides have high transparency in the visible spectral range, chemical and thermal stability and have an optimal refractive index for these purposes [4]. Thus, deposition of a REE film on the silicon surface makes it possible to reduce the spectral coefficient of light reflection from the silicon surface to 0.01…1.2% and increase the photocurrent value of the short-circuit of a silicon photoelectric converter by more than 50% [5-7].

This interest in the search for alternative oxides was produced by the fact that the reduction in the scale of silicon MIS devices is accompanied by a decrease in the length of the channel and the thickness of the gate insulator [11]. Reducing the thickness of the traditional SiO_2 oxide to 10…15°Å is attended with an unacceptably high leakage current [11]. Reducing the leakage current through the gate dielectric is achieved by replacing silicon dioxide with the so-called "alternative dielectrics" (dielectrics with high dielectric permittivity – high-k dielectrics) [11]. The use of alternative dielectrics allows increasing the physical thickness of dielectrics and thereby suppress the tunnel current [11-13]. Another application of alternative dielectrics is associated using them in the memory capacitor of the respective cell [13]. Recently, it has been proposed to use alternative dielectrics to increase fast acting of FLASH (fast) memory [13].

An important requirement for optical coatings of semiconductor devices is the possibility to prepare an interface with semiconductor possessing low

recombination losses. So, in REE oxide/Si structures, the oxide/silicon interface is sharp and does not contain an extended disrupted transition layer [1], in contrast to the cases of formation of solid solutions at the hetero-interface with silicon [14]. In [1], the absence of a "thick" broken transitional layer is associated with relatively low temperatures for producing the dielectric films based on REE oxides, which do not cause significant mechanical stresses.

It was shown in [4] that using the erbium oxide antireflective film makes it possible to increase the integrated sensitivity of a silicon photoelectric converter by 30…32% in the region of 400 to 1100 nm.

Direct formation of REE oxides on the surface of a semiconductor substrate is difficult owing to the high coefficient of interdiffusion [8]. In this case, the structural, optical and electrical characteristics of Er_2O_3 films depend critically on the methods and conditions of their production, on subsequent processing, and on the type of substrates used [5, 9, 10, 15, 16].

In this work, comparative studies of Er_2O_3 films formed by the rapid thermal annealing (RTA) method on silicon carbide substrates and in the presence and absence of a porous SiC layer were performed.

2. Samples and measurement procedure

The oxide Er films on the surface of crystalline silicon carbide were prepared by oxidizing thin metallic Er films deposited on SiC by thermal sputtering by using rapid thermal annealing at the temperature 350 °C for 1, 3 and 5 s.

To obtain the Er_2O_3/por-SiC/SiC structure, a por-SiC layer was first deposited on a silicon carbide substrate. Porous silicon carbide was created by anodic etching of silicon carbide in a hydroalcoholic solution of hydrofluoric acid H_2O:HF:C_2H_5OH = 1:1:2, the current density was 20 mA/cm^2, and the etching time was 5 min. The material was then processed in an etchant KNO_3 + KOH to open the pores. Formation of the Er_2O_3 film was carried out in several technological stages. On the surface of porous silicon carbide, an erbium film was deposited using the thermal deposition method. Then, the samples of porous SiC with a deposited metal film were annealed in vacuum at the temperature 800 °C for 8 min, after which they were subjected to RTA in atmosphere of dry oxygen at the temperature 400 °C for 1, 3, and 5 s.

Transmission and photoluminescence (PL) spectra were measured in all the samples. Absorption and PL spectra were measured with SDL-2 set up in the region λ = 400…800 nm. As a source of continuous spectrum for obtaining the transmission spectra, the spectral lamp SIRSh-200 was used. To excite the PL spectra, we used radiation from a nitrogen laser (λ_{ex} = 337 nm). All optical measurements were carried out at room temperature. The atomic composition of the structures under investigation was measured using the Auger spectrometer LAS-2000 with layer-by-layer etching of samples with 1-keV Ar^+ ions.

3. Experimental results and discussion

A comparison of the thicknesses of the oxide layers determined using Auger spectroscopy showed that both in the presence of a buffer layer and in its absence layers of about the same thickness 100 nm were formed.

Fig. 1 shows the image of the porous surface of the sample (1) and the Er_2O_3 film (2), obtained by scanning electron microscopy.

Fig. 2 shows the atomic profiles of hetero-compositions formed by erbium oxide on SiC substrate in the presence and absence of the por-SiC buffer layer in the interface region of the oxide layer/substrate.

As can be seen from Fig. 2, the ratio of the components of the Er oxide practically corresponds to the stoichiometric composition of the erbium sesquioxide: $N_O/N_{Er} \approx 1.6…1.7$ for oxides formed directly on the crystalline SiC substrate and $N_O/N_{Er} \approx 1.3…1.6$ for oxides formed on the SiC substrate in the presence of a por-SiC buffer layer.

As can be seen from Fig. 2, the chemical composition of the transition regions 'oxide film – substrate' differs from the bulk of the oxides. Here, a sharper oxide film/substrate interface is observed, when the Er_2O_3 is formed directly on the crystalline substrate.

As follows from the Auger spectrometry data, when growing erbium oxides, heat treatment makes it possible to form oxide Er layers with uniform thickness, composition of which would be close to the stoichiometric one. The observed changes in the composition of oxide phases in the near-boundary layers and their extent are related with the conditions for preparing the oxide.

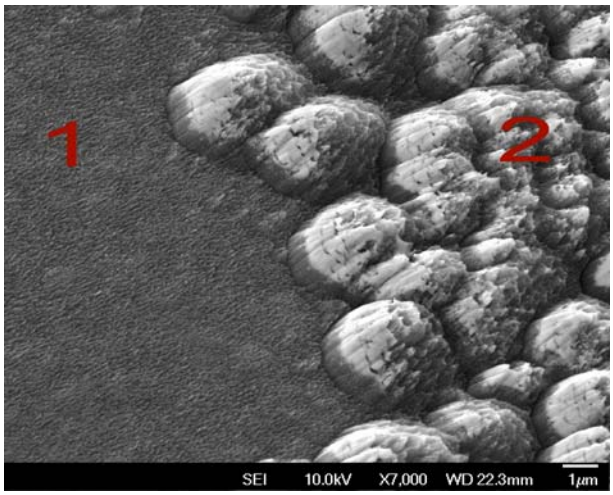

Fig. 1. Image of the Er_2O_3/por-SiC/SiC structure: *1* – porous layer, *2* – Er_2O_3 film, which was obtained by scanning electron microscopy.

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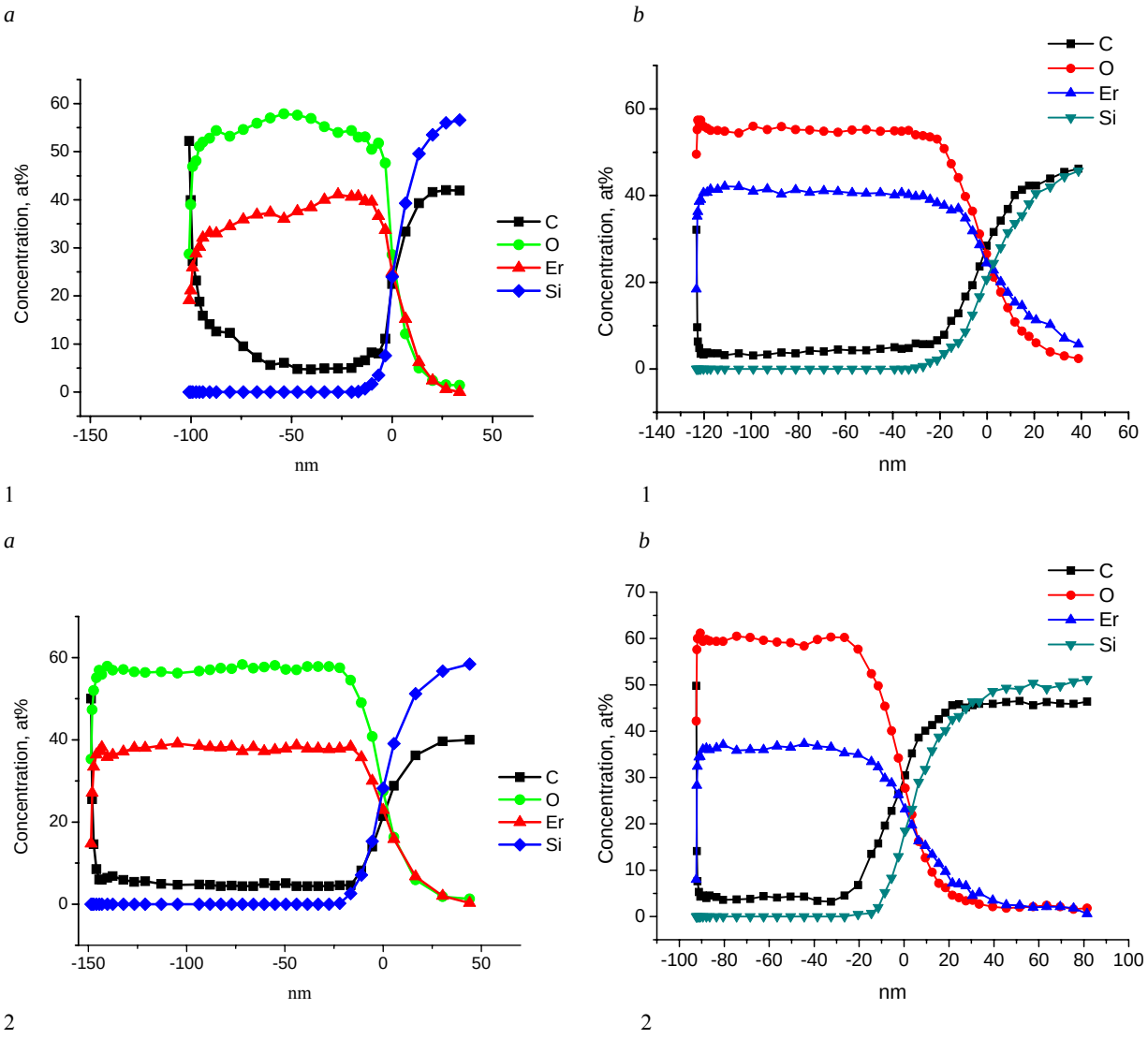

Fig. 2. Element content in atomic percentages in the samples Er_2O_3/SiC (*a*) and Er_2O_3/por-SiC/SiC (*b*). RTA time 1 s (*1*), 5 s (*2*).

As it was shown earlier, the increase in RTA time also leads to an increase in the optical transmission in the spectral interval 400…800 nm both in the 6H-SiC/Er_2O_3 structures [7] and in the SiC/por-SiC/Er_2O_3 ones [18, 19]. The increase in the optical transmission for oxidizable erbium films is caused by the increase in the proportion of the oxide Er film with the stoichiometric composition with respect to the under-oxidized metal layer, which is confirmed by Auger spectroscopy data [17-19].

It should be noted that the PL spectra for structures formed on identical substrates do not depend on the time of RTA and are almost identical, but they vary greatly with changing the substrate structure. Fig. 3 shows the characteristic photoluminescence spectra of Er_2O_3/SiC and Er_2O_3/por-SiC/SiC structures normalized to the maximum of the band.

As can be seen from Fig. 3, in the PL spectra of both Er_2O_3/SiC and Er_2O_3/por-SiC/SiC structures, a broad band with a maximum near 630 nm is observed. In the literature [13-20], this PL band is associated with radiative transitions at the centers of an impurity (nitrogen) – defect or an impurity – vacancy (usually the vacancy of carbon is considered). In [24], this band is related with recombination processes caused by the presence of defects near the surface of a silicon carbide crystal. Apparently, the substantial broadening the PL band in Er_2O_3/por-SiC/SiC structures is responsible for this particular presence of defects at the Er_2O_3/por-SiC interface. In addition, as it was noted in [18], the appearance of a broad PL band of por-SiC is associated with impurity states that are formed on the surface of the sample during its processing and due to products of chemical reactions when etching [25-27]. According to

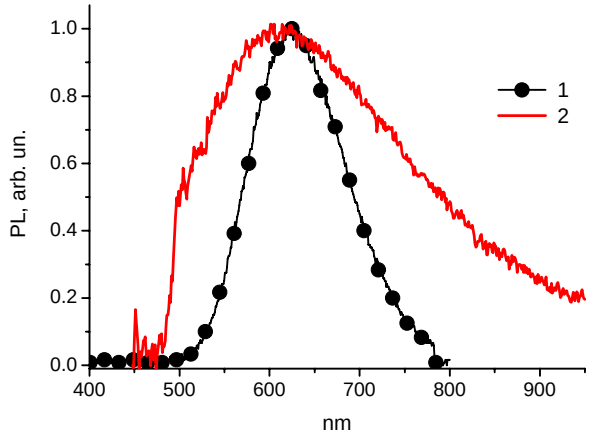

Fig. 3. PL spectra for Er_2O_3/SiC (*1*) and Er_2O_3/por-SiC/SiC (*2*) structures.

[25-27], one of the reasons for appearance of PL in por-SiC are surface states caused by the presence of impurities, surface defects, complex compounds (such as oxides and siloxenes) or saturation of Si–H or C–H bonds. When analyzing the PL spectra of multilayer structures, it should be taken into account that the integrated PL spectrum of such a structure is caused by contribution of both the PL spectra of the oxide film and that of the substrate. In this case, the characteristics of the PL spectrum of the substrate will also depend on the transmission spectrum of the oxide film in the region of the exciting radiation and in the luminescence region of substrate. The previously noted increase in the degree of transparency of Er oxide films with increasing time of RTA does not lead to any change in the spectral characteristics of PL structures. Thus, an analysis of the PL spectra of Er_2O_3/SiC and Er_2O_3/por-SiC/SiC structures shows that the spectral composition of the PL band of these structures is mainly due to the contribution of the substrate.

Broadening the PL band in the structure containing the por-SiC layer, in comparison with the PL band of the Er_2O_3/SiC structure, is probably caused, as in the case of PL of proper por-SiC [25-27], by the presence of defects at the Er_2O_3/por-SiC interface, which correlates well with the Auger spectroscopy data indicating a blurring of the oxide film/substrate interface in the presence of a porous buffer layer (Fig. 2).

4. Conclusions

Analysis of the obtained experimental data has shown that the RTA method for obtaining oxide Er layers on the SiC surface allows creating thin oxide films with a composition close to the stoichiometric one. At the same time, using the RTA method to form Er_2O_3 films on the surface of a porous layer leads to a blurring of the oxide film/substrate interface. At the same time, an increase in the RTA time leads to improvement in the composition of the oxide film in both cases.

References

1. Fedorenko Y.G., Sverdlova A.M., Malinin A. Study of the dynamical characteristics of an insulator-semiconductor interface. *Semiconductors*. 1998. **32**, Issue 11. P. 1190–1195.
2. Korolevich L.N., Borisov A.V., Prokopenko A.S., Minyailo A.N. CV-investigation of the electrophysical parameters of thin CeO_2 films in the Al-CeO_2-n-Si-Al MIS structure. *Elektronika I Sviaz'*. Tematich. vypusk "Problemy elektroniki". 2008. Part 1. P. 35-37 (in Russian).
3. Rozhkov V.A., Trusova A.Yu., Berezhno I.G. Energy barriers and trapping centers in silicon metal-insulator-semiconductor structures with samarium and ytterbium oxide insulators. *Techn. Phys. Lett*. 1998. **24**, Issue 3. P. 217–219.
4. Rodionov M.A., Rozhkov V.A. Antireflection properties of erbium oxide films. *Techn. Phys. Lett*. 2005. **31**, Issue 1. P. 77–78.
5. Rodionov M.A., Rozhkov V.A. Silicon passivated by insulating erbium oxide films. *Techn. Phys. Lett.* 2005. **31**, Issue 2. P. 115–116.
6. Anoshin Yu.A., Petrov A.I., Rozhkov V.A., Romanenko N.N., Shalimova M.B. Rare-earth oxide antireflection coatings for silicon photoelectric devices. *Pis'ma v ZhTF*. 1992. **18**, No. 10. P. 54-58 (in Russian).
7. Rozhkov V.A., Petrov A.I. Accumulation of charge in silicon MIS-structures with dysprosium oxide dielectrics under the influence of UV radiation. *Izvestia Vuzov. Fizika*. 1994. № 7. P. 99–104 (in Russian).
8. Hubbard K.J., Schlom D.G. Thermodynamic stability of binary oxides in contact with silicon. *J. Mater. Res*. 1996. **11**, No. 11. P. 2757–2776.
9. Al-Kuhaili M.F., Durrani S.M.A. Optical properties of erbium oxide thin films deposited by electron beam evaporation. *Thin Solid Films*. 2007. **515**, No. 5. P. 2885–2890.
10. Mikhelashvili V., Eisenstein G., Edelman F., Brener R., Zakharov N., Werner P. Structural and electrical properties of electron beam gun evaporated Er_2O_3 insulator thin films. *J. Appl. Phys*. 2004. **95**, No. 2. P. 613–620.
11. Gritsenko D.V., Shaimeev S.S., Atuchin V.V., Grigor'eva T.I., Pokrovskii L.D., Pchelyakov O.P., Gritsenko V.A., Aseev A.L., Lifshits V.G. Two-band conduction in TiO_2. *Phys. Solid State*. 2006. **48**, Issue 2. P. 224–228.
12. Kingon A.I., Maria J.-P., Streiffor S.K. Alternative dielectrics to silicon dioxide for memory and logic devices. *Nature*. 2000. **406**. P. 1032–1038.
13. Wilk G.D., Wallace R.M., Anthony J.M. High-k gate dielectrics: Current status and materials properties considerations. *J. Appl. Phys*. 2001. **89**, No. 10. P. 5243–5275.
14. Sapaev B., Saidov A.S., Sapaev I.B., Bacherikov Yu.Yu., Konakova R.V., Okhrimenko O.B., Dmit-

ruk I.N., Galak N.P. Spectroscopy of solid solutions $(Si_2)_{1-X}(ZnS)_X$. *SPQEO*. 2005. **6**, № 3. P. 16–18.
15. Alfian Noviyanto, Dang-Hyok Yoon. Rare-earth oxide additives for the sintering of silicon carbide. *Diamond and Related Material*. 2013. **38**. P. 124–130.
16. Cho Y.S., Heo J.S., Kim J.C., Moon S.H. Monitoring of an interlayer between Si(100) and a TiO_2 layer formed during cyclic CVD. *Chemical Vapor Deposition*. 2006. **12**, No. 11. P. 659–664.
17. Bacherikov Yu.Yu., Dmitruk N.L., Konakova R.V. et al. Effect of rapid thermal annealing on the properties of thin dielectric films of gadolinium, titanium, and erbium oxides on the silicon carbide surface. *Techn. Phys.* 2007. **52**, No. 2. P. 253–257.
18. Berezovska N.I., Bacherikov Yu.Yu., Konakova R.V., Okhrimenko O.B., Lytvyn O.S., Linets L.G., Svetlichnyi A.M. Characterization of porous silicon carbide according to absorption and photoluminescence spectra. *Semiconductors*. 2014. **48**, No. 8. P. 1028–1030.
19. Bacherikov Yu.Yu., Konakova R.V., Okhrimenko O.B. et al. Effect of por-SiC buffer layer on the parameters of thin Er_2O_3 layers on silicon carbide substrates. *Mater. Sci. Eng.* 2015. **81.** P. 012019.
20. Gorban' I.S., Krokhmal'A.P. The impurity optical absorption and conduction band structure in 6H-SiC. *Semiconductors*. 2001. **35**, Issue 11. P. 1242–1248.
21. Safaraliev G.K., Émirov Yu.N., Kurbanov M.K., Bilalov B.A. Spectral shift of photoluminescence bands of the $(SiC)_{1-x}(AlN)_x$ epitaxial films due to laser annealing. *Semiconductors*. 2000. **34**, Issue 8. P. 891–893.
22. Patrick Lyle, Choyke W.J. Photoluminescence of radiation defects in ion-implanted 6H-SiC. *Phys. Rev. B*. 1972. **5**, No. 8. P. 3253–3259.
23. Choyke W.J., Patrick Lyle. Photoluminescence of radiation defects in cubic SiC: Localized modes and Jahn-Teller effect. *Phys. Rev. B*. 1971. **4**, No. 6. P. 1843–1847.
24. Gorban' I.S., Rud'ko S.N. Optical properties of silicon carbide crystals. Fizika Tverd. Tela. 1963. **5**, Issue 5. P. 1368–1372 (in Russian).
25. Ki-Hwan Lee, Seung-Koo Lee, Ki-Seok Jeon. Photoluminescent properties of silicon carbide and porous silicon carbide after annealing. *Appl. Surf. Sci.* 2009. **255**, No. 8. P. 4414–4420.
26. Rittenhouse T.L., Bohn P.W., Hossain T.K., Adesida Ilesanmi, Lindesay J., Marcus A. Surface-state origin for the blueshifted emission in anodically etched porous silicon carbide. *J. Appl. Phys.* 2004. **95**, No. 2. P.490–496.
27. Higashi E., Tajima M., Hoshino N., Hayashi T., Kinoshita H., Shiomi H., Matsumoto S. Defect observation in SiC wafers by room-temperature photoluminescence mapping. *Mater. Sci. in Semiconduct. Process.* 2006. **9**, Issues 1-3. P. 53–57.