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Changes in Characteristics of Gadolinium, Titanium, and Erbium Oxide Films on the SiC Surface under Microwave Treatment

Yu. Yu. Bacherikov[a], R. V. Konakova[a], V. V. Milenin[a], O. B. Okhrimenko[a]^, A. M. Svetlichnyi[b], and V. V. Polyakov[b]

[a]*Lashkarev Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, pr. Nauki 41, 03028 Kiev, Ukraine*
^*e-mail: olga@isp.kiev.ua*
[b]*Taganrog State Radio Engineering University, Nekrasovskyi 44, Taganrog, 347928 Russia*
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Abstract—The effect of microwaves on properties of Ti, Gd, and Er oxide films deposited on silicon carbide was studied using optical absorption and photoluminescence methods. The atomic composition of films was analyzed in relation to the microwave treatment time. It was shown that exposure to microwaves results in the appearance of an additional band in the photoluminescence spectra of the structures under study. It was shown that microwave treatment leads to an increase in the sample transmittance, which indicates an improvement in integrated characteristics of structures.

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1. INTRODUCTION

The operating conditions of semiconductor circuitry dictate requirements for its stability to various exposures. Therefore, one of the most important problems of modern microelectronics is the study of the effect of various external factors on properties of silicon-carbide-based semiconductor materials and devices to identify their property evolution (degradation) mechanisms. It is also important to search for new technological methods of the intentional control of properties of such materials and devices. In particular, it is urgent to study the effect of microwaves on device structures based on silicon carbide.

Precisely the state of intrinsic and impurity defects controls, to a large extent, the operational and degradation characteristics of semiconductor devices. It is known that exposure to microwaves leads in some cases to catastrophic failures of device structures and final products (diodes, transistors, and integrated circuits) [1]. At the same time, there are published data on microwave-enhanced effects of defect gettering and structural relaxation in semiconductor materials [2–4]. Moreover, the presence of dielectric films on the semiconductor surface can reduce defect formation caused by microwaves [5], which promotes improvement of device structure quality. For example, high thermal stability, large permittivities, and relative simplicity of technological processes of growth of films of some rare-earth element oxides make them promising to obtain insulating layers used in technology of some semiconductor devices and integrated circuits (ICs). Such films are efficiently used as antireflection coatings of silicon photoelectric devices [6]. In addition, as shown in [6], erbium oxide film deposition on silicon increases the nonequilibrium-carrier lifetime and decreases the surface recombination velocity, which indicates the high efficiency and promise of application of insulating erbium oxide films as passivating coatings of silicon active elements and ICs.

The goal of this paper is to study the effect of microwave treatment on optical properties of thin oxide layers of titanium, gadolinium, and erbium obtained by rapid thermal annealing (RTA) on the surface of n-6H-SiC single crystals grown by the Lely method.

2. EXPERIMENTAL

Rare-earth-metal films were deposited on SiC by thermal sputtering. Metal oxide films were obtained by oxidation of thin Ti, Er, and Gd films in a dry oxygen medium using a vacuum pulsed thermal setup ITO-18MV [7] at $T = 623$ K for 1, 3, and 5 s. The thickness of silicon carbide itself was 530 ± 10 μm.

The oxide film thickness was estimated by multibeam ellipsometry as 35–65, 45–70, and 100–145 nm for titanium, gadolinium, and erbium oxide films, respectively [8].

Transmission and photoluminescence (PL) spectra were measured for all samples in the range $\lambda = 370$–800 nm. PL spectra were measured from the oxide film side using an SDL-2 setup. PL spectra were excited using a nitrogen laser ($\lambda_{exc} = 337$ nm). Absorption spec-

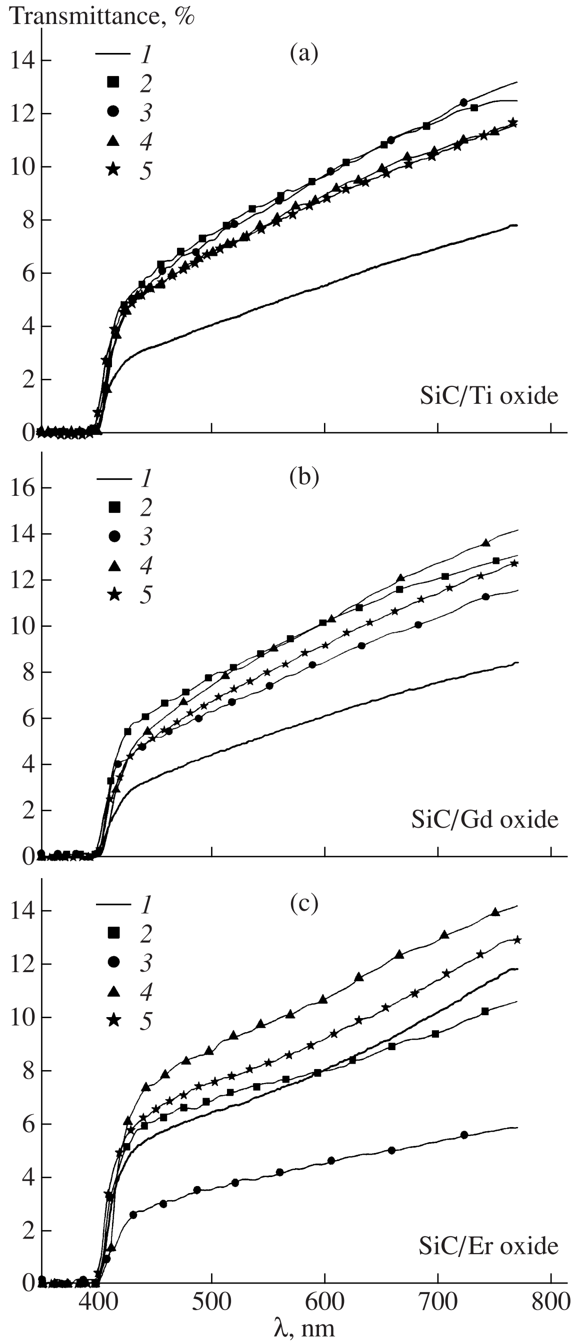

Fig. 1. Transmittance spectra of the SiC/oxide film structures: (a) Ti oxide, (b) Gd oxide, and (c) Er oxide. (*1*) initial sample and samples with total microwave treatment times of (*2*) 1, (*3*) 2, (*4*) 3, and (*5*) 8 s.

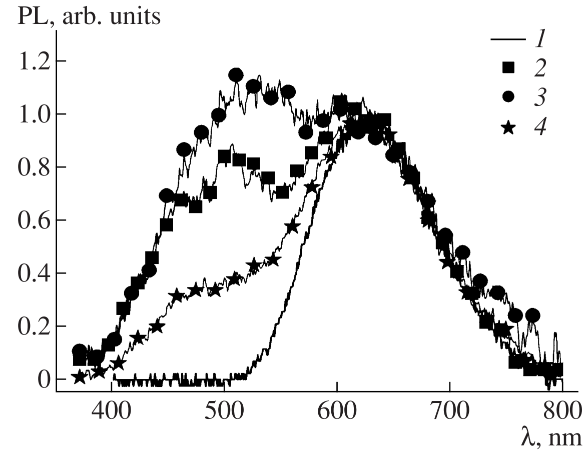

Fig. 2. Photoluminescence spectra of the SiC/metal oxide film structures before ((*1*) initial sample) and after microwave treatment ((*2*) SiC/Ti oxide, (*3*) SiC/Gd oxide, and (*4*) SiC/Er oxide). The total microwave treatment time is 8 s.

tra were measured using a SPECORD UV VIS setup. All optical measurements were performed at room temperature.

Microwave treatment was carried out in a magnetron working chamber with frequency $f = 2.45$ GHz and specific power of 0.04 W/cm^3. The total microwave annealing time was 8 s. The time of single microwave irradiation of the sample was from 1 to 5 s.

3. RESULTS AND DISCUSSION

Figure 1 shows the transmission spectra of the structures under study. As seen in Fig. 1, the transmittance increased for all samples after microwave irradiation when the total microwave treatment time was 8 s. A similar effect of increasing the transmittance after microwave exposure is observed for SiC/SiO_2 structures [9]. However, although the general tendency is an increase in the transmittance with the microwave treatment time, the transmission spectra of SiC/oxide film structures contain features caused by the oxide film composition. The transmission spectra for the structures with Ti and Gd oxide films (Figs. 1a and 1b) qualitatively similarly depend on the microwave exposure time, and an increase in the transmittance for the structures with Ti and Gd films is observed even at a minimum microwave exposure time. The dependence of the transmission spectra of SiC/(Er oxide film) structures on the microwave exposure time is nonmonotonic (Fig. 1c).

Figure 2 shows the PL spectra measured from the side of the oxidized metal film before (Fig. 2, curve *1*) and after (Fig. 2, curves *2–4*) irradiation with microwaves; the total microwave exposure time was 8 s. For convenience, the spectra are normalized by the PL band maximum. The PL spectral characteristics of all samples before microwave irradiation are identical (Fig. 2, curve *1*). As seen in Fig. 2, the PL spectra contain a band with a maximum in the region $\lambda = 630$ nm before and after microwave treatment. In the available publications [10–12], such a PL band is associated with radiative transitions at impurity–defect centers. In [13], this band is related to recombination processes caused by defects near the silicon carbide crystal surface. Microwave treatment results in the appearance of an additional broad band in the PL spectrum of the structure under study. As seen in Fig. 2, the peak position of this band depends on the oxide film composition. For exam-

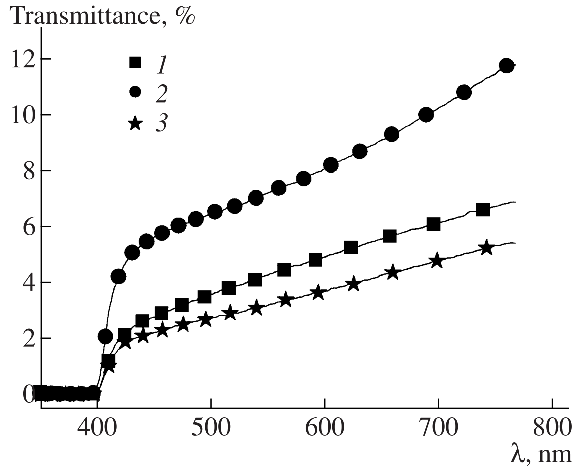

Fig. 3. Transmittance spectra of the SiC/oxide structures after microwave treatment for 8 s: (*1*) SiC/Ti oxide, (*2*) SiC/Gd oxide, and (*3*) SiC/Er oxide.

ple, for the SiC/(Ti oxide film), SiC/(Gd oxide film), and SiC/(Er oxide film) structures, the peak positions are in regions of 520 nm (Fig. 2, curve *2*), 500 nm (Fig. 2, curve *3*), and 470 nm (Fig. 2, curve *4*), respectively. In the previous publications, the appearance of the additional band in the region of 400–500 nm in PL spectra of silicon carbide is related to luminescence centers caused by intrinsic defects [14] or stoichiometry violation in silicon carbide crystals [15]. Konstantinov et al. [16] consider the center causing the appearance of the short-wavelength PL band ($\lambda_{max} \approx 500$ nm) to be a defect cluster. As seen in Fig. 2, the ratio of the intensity of the additional short-wavelength band to the intensity of the PL fundamental band (with a maximum in the region of 630 nm) depends on the oxide film composition, and the intensity of this band is proportional to the film transmittance (Fig. 3).

The absorption and PL spectra of the analyzed structures are specific integral characteristics of the structure. Since erbium, gadolinium, and titanium oxide films are transparent in the region under study [17–19], and the penetration depth of excitation laser radiation for *n*-SiC single crystals is on the order of 10 nm, it can be assumed that the PL spectrum is mostly caused by the contribution of silicon carbide at the SiC/(oxide film) interface. Hence, the features of changes in the PL spectra of the entire structure will be first of all caused by changes in the properties of the oxide film and silicon carbide at the SiC/(metal oxide film) interface due to exposure to microwaves exposure. At the same time, the transmission spectrum is sensitive to both surface and bulk characteristics of the entire structure. For example, the absorption edge of each individual sample in the absorption spectra will be controlled by the structure component with a maximum absorbance in a given region.

To assess the thermal effect of microwave radiation on the sample, let us estimate the temperature change ΔT due to such exposure. Since the oxide layer does not absorb microwaves [20], the sample can be heated only due to microwave absorption in semiconductor. Let us assume that the sample completely absorbs microwaves; then the maximum possible heating temperature of the sample can be calculated by the formula

$$\Delta T = \frac{E}{VC\rho},$$

where C is the sample specific heat, ρ is the sample density, V is the sample volume (in the case at hand, the average sample volume is $\bar{V} = 0.0125$ cm^3), $E = Wt$ is the energy which the sample can get for the time t, $W = PV$ is the microwave power per sample volume, and P is the specific microwave power. For silicon carbide, $C = (620–750)$ J/(kg K) and $\rho = 3170$ kg/m^3 were used [20]. We find that the sample temperature can change by $\Delta T = 0.02$ K for an irradiation time of 1 s. Thus, we can eliminate the contribution of the thermal mechanism in the model for explaining the observed changes in properties of the oxide film and silicon carbide at the SiC/(metal oxide film) interface caused by microwave irradiation.

The increase in the sample transmittance after microwave treatment can be explained by several causes. One is that the oxide film stoichiometry changes during microwave treatment, due to which the light scattering loss at the (oxide film)/SiC interface decreases. Another is a change in the gradient of internal mechanical stresses and a decrease in the number of internal interfaces caused by dislocation planes in the silicon carbide bulk, which can also decrease the light scattering loss in the sample. However, additional studies are required for more adequate interpretation of the contribution of the microwave effect on SiC bulk properties to differentiate the effects caused by the SiC substrate itself and stresses at the film/substrate interface

The appearance of the additional impurity–defect PL band due to microwave irradiation of the oxide film is in good agreement with Auger spectrometry data. Figure 4 shows the characteristic distributions of elements in these structures, measured by Auger electron spectroscopy before and after microwave treatment. As seen in Fig. 4, the (oxide film)/SiC interface is spread after microwave treatment for all the structures under study (Fig. 4).

In the film–substrate structures, observed stresses are due to mismatching the layer and substrate lattice constants [21]. Another no less important factor which causes stresses in heterostructures is the difference between the thermal expansion coefficients of the oxide layer and substrate. Since the oxide layer thickness is smaller than the substrate thickness, stresses in layers will be especially significant. According to [22], local curvature regions at the substrate–film interface are stress concentrators. In this case, dislocation accumula-

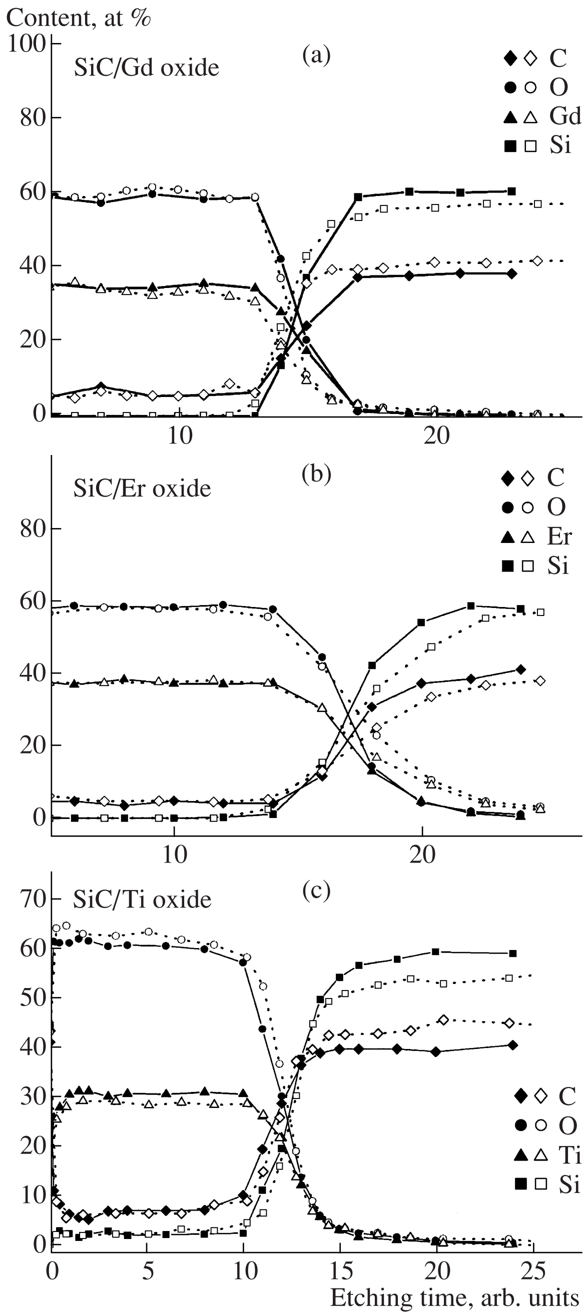

Fig. 4. Element content (at %) in (a) SiC/Gd oxide, (b) SiC/Er oxide, and (c) SiC/Ti oxide. Solid curves and closed symbols correspond to initial samples, dashed curves and open symbols correspond to samples after microwave treatment.

tion in the surface layer is more intense than in the sample bulk [22]. The more so with the factors promoting an increase in the dislocation mobility, e.g., microwave exposure.

The presence of stresses has a negative effect on the structure quality: their strength is lowered and degradation processes are activated in devices fabricated from such structures.

The appearance of the additional PL band (Fig. 2) associated with the impurity–defect complex [14–16] is caused by localization of structural defects stimulated by microwave irradiation and mechanical stresses at the interface SiC/(oxide film). The change in the peak position of the additional PL band is caused by different biaxial stresses at the SiC/(oxide film) interface and depends on the metal oxide film parameters [21]. The observed insignificant shift of the additional PL band, depending on the oxide film composition indicates a change in stresses. Since the peak position of the additional PL band almost coincides with the peak position of the similar PL band in silicon carbide when the erbium oxide film is deposited on the silicon carbide surface [16], it can be concluded that erbium oxide films induce minimum stresses at the SiC/(oxide film)interface. The shift of the peak position of the additional PL band to longer wavelengths (Fig. 2) suggests the occurrence of tensile stresses when titanium or gadolinium oxide films are deposited on the silicon carbide surface.

However, further studies are required for more unambiguous identification of the nature of the additional short-wavelength band in PL spectra. The unchanged peak position of the fundamental PL band (λ_{max} = 630 nm) indicates localization of centers causing this band in the SiC crystal volume.

4. CONCLUSIONS

Thus, the described results show the significant effect of microwave irradiation on the SiC/(titanium (gadolinium or erbium)) oxide film structure parameters. Despite the formation of structural defects at the SiC/(oxide film) interface, which is suggested by the appearance of the additional band in the PL spectra of the structures under study, there is a tendency towards improvement of the integrated characteristics of the structure, which manifests itself in an increase in the sample transmittance.

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