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Sensors

Comparison of properties inherent to thin titanium oxide films formed by rapid thermal annealing on SiC and porous SiC substrates

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Abstract. The comparative analysis of optical characteristics inherent to TiO_2/SiC and TiO_2/por-SiC/SiC structures has been performed. It has been shown that, in these structures regardless of the substrate structure, formation of TiO_2 layers with approximately the same width 60 nm takes place. In this case the TiO_2 film composition is close to the stoichiometric one. At the same time, the presence of an additional porous layer in the TiO_2/por-SiC/SiC structure leads to blurring the oxide film – substrate interface but promotes an increase in the intensity of the Raman scattering signal from the oxide film.

Keywords: thin titanium oxide films, SiC substrates, interface, porous layer.

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1. Introduction

The continuing interest in silicon carbide as a material for fabrication of semiconductor devices operating under extreme conditions is explained by a combination of such factors as a wide forbidden band, high electron mobility, chemical and mechanical resistance [1-3]. All this determines the possibility to use it in devices capable to operate at elevated temperatures, elevated irradiation doses, with high speed and high stability of their properties in time.

At present, the urgent task for high-temperature electronics based on silicon carbide is to develop stable high-quality dielectric layers, including those based on titanium oxide films. Despite the wide range of technological possibilities for creation of oxide metal films (from anodic to oxidation in air or in the atmosphere of oxygen, water and water vapor, in carbon dioxide or in various other gas mixtures [4]), the search for well-controlled, fast methods of formation with high reproducibility of parameters of oxide metal films with set properties are being performed up to date.

It is known that the structural defects of a semiconductor substrate, which penetrate into a thin film grown on this substrate during a high-temperature process, can significantly worsen the characteristics of devices. One way for reducing this effect is to create a porous interlayer between the substrate and epitaxial layer [5, 6]. For example, the layers of porous silicon carbide (por-SiC) are used in complex structures to decrease the concentration of defects at the boundary ‘porous layer – epitaxial film’ [6-10].

In addition, the pore-developed surface makes porous silicon carbide a promising material for sensitive elements of sensors with both the Schottky barriers and MIS structures [11]. The principle of operation of many devices is based on changes in the potential barrier of contact typical for porous SiC with metal or dielectric. In these cases, an important role is played by processes occurring at the boundary of the porous silicon carbide with metallic or dielectric layers.

In this paper, we have performed the comparative studies of TiO_2 films formed by rapid thermal annealing on silicon carbide substrates in the presence and absence of a porous SiC layer.

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2. Samples and experimental procedure

The oxide films TiO_2 were prepared by oxidizing thin Ti metal films by using rapid thermal annealing at T = 323 °C for 1, 3 and 5 s.

To form the SiC/por-SiC/TiO_2 structure on a silicon carbide substrate, a por-SiC layer was preliminarily prepared. Porous silicon carbide was created using anodic etching of silicon carbide in a hydro-alcohol 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. Then, the material was processed in the etchant KNO_3+KOH to open the pores. Formation of the oxide film TiO_2 was carried out in several technological stages. On the surface of porous silicon carbide, a titanium film was deposited using a thermal deposition method. Then, the samples of porous SiC with introduced Ti were annealed in vacuum at 1350 °C for 8 min, after which they were subjected to rapid thermal annealing in atmosphere of dry oxygen for 30 s at the temperatures 700, 900 and 1000 °C [12, 13].

The thickness of the oxide layers was determined using the method of multibeam monochromatic ellipsometry. On all the samples, morphology of the coating was studied using the atomic force microscope NanoScopeIIIa (DJ). The atomic composition of the structures under investigation was measured using the Auger spectrometer LAS-2000, when layer-by-layer etching the samples with 1-keV Ar ions was used.

The micro-Raman spectra of the samples were measured at room temperature in the backscattering geometry by using the Horba Jobin Yvon T64000 spectrometer with a confocal microscope (100× lens, 0.90 diaphragm) and cooled CCD detector. The Raman spectra were excited by an Ar-Kr laser λ_{exc} = 488.0 nm). In Raman studies, the laser beam was focused into a beam of diameter <1 µm. The accuracy of determining the frequency position of the phonon lines was 0.15 cm^{-1}.

3. Experimental results and discussion

Calculation of the thickness of the oxide metal film was carried out using the method of multi-beam monochromatic ellipsometry (operating wavelength λ = 632.8 nm).

Parameters of the films were determined from the model of a single-layer film on a substrate as a result of fitting the calculated angular dependences of the polarization angles ψ and Δ to the experimental dependences $\psi(\varphi)$ and $\Delta(\varphi)$ by using the computer program for minimizing the special objective function $S(x)$ [14].

$$S(x)=\frac{1}{N}\sum_{i=1}^{N}\left[\frac{\left(\psi(x,\varphi_i)-\psi'(\varphi_i)\right)^2}{\left(\delta\psi'(\varphi_i)\right)^2}+\frac{\left(\Delta(x,\varphi_i)-\Delta'(\varphi_i)\right)^2}{\left(\delta\Delta'(\varphi_i)\right)^2}\right]\times$$

$$\times\sum_{i=1}^{N}\left[\left(\delta\psi'(\varphi_i)\right)^2+\left(\delta\Delta'(\varphi_i)\right)^2\right],$$

where $\psi'(\varphi_i)$ and $\Delta'(\varphi_i)$ are the experimentally measured polarization angles at an angle of incidence φ_i; $\psi'(x, \varphi_i)$ and $\Delta'(x, \varphi_i)$ are the results of calculation of the direct problem of ellipsometry for the angle φ_i and vector of optical parameters and layer thicknesses x; $\delta\psi'(\varphi_i)$ and $\delta\Delta'(\varphi_i)$ – measurement errors, N – total number of the used angles of incidence.

As control data, the values of absorption and refractive indexes for silicon carbide were calculated. The refractive index n_{SiC} calculated on the basis of the ellipsometric measurement data is in good agreement with the expected averaged value (without account of anisotropy), and the absorption index k_{SiC} for λ = 632.8 nm is very small, which is a confirmation of the accuracy inherent to the method.

A comparison of the thicknesses of the oxide layers determined using the method of multi-beam ellipsometry has shown that, both in the case of the presence of a buffer layer and in its absence, layers of approximately the same width 60 nm were formed, which correlates with the Auger spectrometry data.

Figs 1 (upper and lower) show AFM images of oxide titanium films on single-crystal and porous substrates, respectively. As can be seen from Fig. 1, the oxide film has an inhomogeneous character and granular structure.

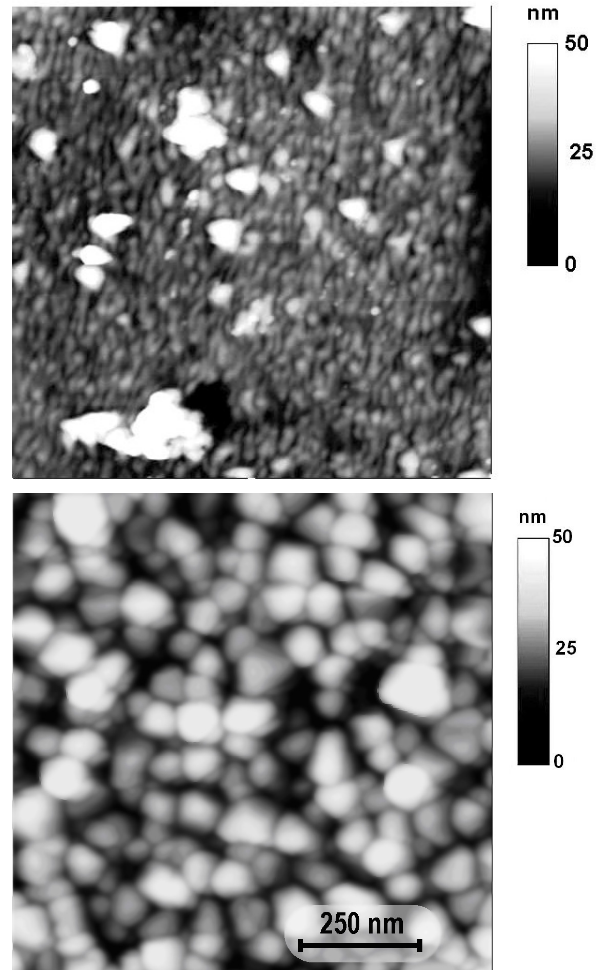

Fig. 1. AFM images of the surface of the SiC/TiO_2 (upper) and SiC/por-SiC/TiO_2 (lower) structures.

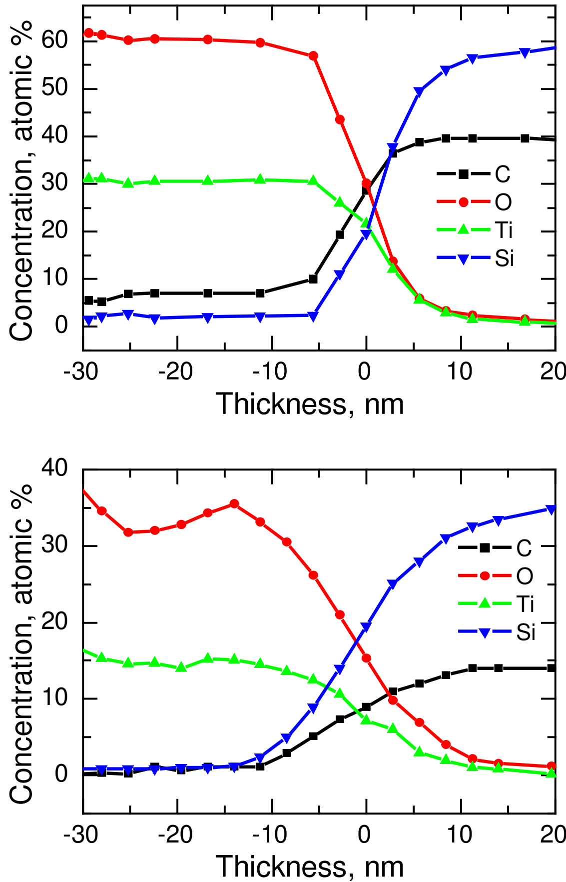

Fig. 2. The contents of elements in atomic percentages in the SiC/TiO_2 (upper) and $SiC/por-SiC/TiO_2$ (lower) structures.

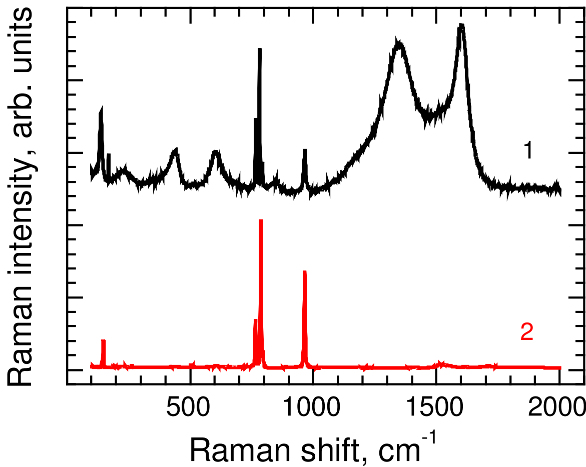

Fig. 3. Raman spectra for the SiC/TiO_2 (*1*) and $SiC/por-SiC/TiO_2$ (*2*) structures.

Fig. 2 shows the atomic profiles of heterostructures formed by titanium oxide on the SiC substrate in the absence and presence of a por-SiC buffer layer at the oxide-semiconductor interface.

According to [15, 16], the phase equilibrium in the titanium-oxygen system is characterized by the presence of several phases: TiO, Ti_2O_3, TiO_2. Moreover, the TiO_2 phase can be available in one of three modifications: anatase, brookite and rutile [17, 18]. The low-temperature modification – anatase – turns into rutile when heated. Typically, this transition to the rutile modification takes place within the temperature range from 650 to 900 °C. The second modification of titanium dioxide – brookite – turns also into rutile when heated to ~1000 °C. In this case, the defect structure of the rutile itself depends essentially on the processing temperature [15, 16].

As can be seen from Fig. 2, the ratio of the Ti oxide components for the oxides, which form directly on the SiC crystal substrate and in the presence of the por-SiC buffer layer, is close to the stoichiometric composition of titanium dioxide: $N_O/N_{Ti} \approx 1.98$ and $N_O/N_{Ti} \approx 2.2$, respectively.

As it follows from the analysis of the distribution of atomic components (Fig. 2), the stoichiometric composition of these oxide titanium layers corresponds to the modification of titanium dioxide with the rutile structure. At the same time, the chemical composition of oxide film – substrate interface differs from the bulk of oxides (Fig. 2).

As in the case of SiC/Er_2O_3 and $SiC/por-SiC/Er_2O_3$ structures [19], a sharper interface ‘oxide film – substrate’ is observed when the TiO_2 is directly formed on the crystalline substrate.

Fig. 3 shows the Raman spectra for SiC/TiO_2 and $SiC/por-SiC/TiO_2$ structures.

As can be seen from Fig. 3, in the Raman spectra of the $SiC/por-SiC/TiO_2$ structure in the 300…600 cm^{-1} region (Fig. 3, curve *2*), in addition to the lines with the frequencies 262.7, 502.37 and 511.07 cm^{-1} typical for por-SiC, we observe the lines with the frequencies of 435 and 603 cm^{-1} that indicate formation of a titanium oxide film on the por-SiC surface [20, 21], which correlates with the Auger spectrometry data (Fig. 2b). At the same time, in the Raman scattering spectra of the SiC/TiO_2 structure, the lines characteristic for the Raman spectrum of TiO_2 are not observed (Fig. 3, curve *2*), although the Auger spectrometry data indicate the presence of titanium oxide in the thin film structure (Fig. 2a). It is caused by the fact that the intensity of the Raman spectra is proportional to the thickness of the layer, and for a very small thickness of the oxide film the intensity of the Raman signal from the TiO_2 film is very small as compared to that of the signal from the substrate. At the same time, a surface-enhanced Raman scattering signal (SERS) is likely to occur due to the presence of a porous layer, as well as due to the presence of under-oxidized metal particles in it, as evidenced by the blurring of the interface in the $SiC/por-SiC/TiO_2$ structure (Fig. 2b).

In addition to the Raman bands caused by the titanium oxide film on the por-SiC surface, in the Raman spectra of the $SiC/por-SiC/TiO_2$ structure, we observe the lines with the frequencies of 1345 and 1601 cm^{-1} (Fig. 3, curve *2*), which are characteristic for the compounds of carbon [22, 23]. These lines are typical for the graphite phase in por-SiC, the appearance of which is associated with high-temperature annealing of por-SiC [24]. When being thermally treated in vacuum, the surface of SiC

tends to be graphitized during thermal decomposition of SiC and evaporation of Si atoms [24]. It was shown in [24] that graphitization of the por-SiC layer can begin at the temperatures close to 700 °C, and the quasi-amorphous carbon phase of the graphitized type can appear on the pore surface.

4. Conclusions

Thus, regardless of the substrate structure, during the rapid thermal annealing, we have obtained the TiO_2 layers of approximately the same width 60 nm with the composition close to the stoichiometric one. In this case, in the SiC/por-SiC/TiO_2 structures, the graphite phase is formed in the por-SiC/TiO_2 interface, which degrades the quality of the interface. At the same time, the presence of a porous layer makes it possible to enhance the Raman signal from a thin TiO_2 film, which opens the perspective of using the por-SiC buffer layer as a substrate for SERS.

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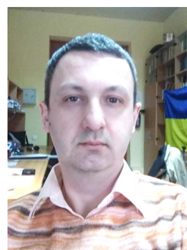

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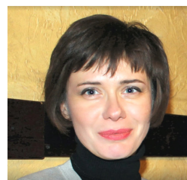

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