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Analysis of the structural composition of a silicon carbide film obtained by high-temperature chemical vapor deposition

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The surface of silicon carbide structures fabricated by high temperature chemical vapor deposition (HTCVD) is investigated. It is shown that a homogeneous polycrystalline film of silicon carbide with a thickness of about 3–6 mkm grows on the surfaces of wafers with orientations 111 and 100. The results of X-ray phase analysis and Raman spectra of samples with silicon carbide are presented. It has been shown that the manufacturing technology of silicon carbide film can lead to the appearance of pure carbon on the surface.

Keywords: silicon carbide, HTCVD, Raman scattering, X-ray phase analysis.

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1. Introduction

Most semiconductor applications today use silicon-based devices. According to advanced technological processes and development methods, silicon crystals of high purity and crystalline quality can be mass produced. However, silicon has many limitations due to its physical properties: silicon is limited to a maximum operating temperature of 150°C and cannot withstand very high voltages. Therefore, SiC may be a better choice due to its superior physical and electrical properties, making it very promising for the next generation of semiconductors for extreme environments, where their application in modern electrical engineering is essential. SiC has many remarkable properties that make it a very promising semiconductor material. Some of the potential applications of silicon carbide relate to high temperature, high frequency and high power electronic devices. Others use wide band gap: UV detectors and even blue light lasers. Light-emitting diodes (LEDs) are commercially produced for several years. Also, some other electronic devices may become commercial in the near future [1–7]. Silicon carbide films can be obtained by various methods: magnetron sputtering of the original target, high-temperature vapor deposition. The latter method is especially interesting because coatings can be grown on several silicon substrates at once, which would be convenient if the method is used in production. However, when growing silicon carbide films by this method, both polycrystalline and single-crystalline films are not always perfect in structure.

2. Coating manufacturing by HTCVD method

In this paper the HTCVD process of growing the SiC film is ensured due to the functional interconnections of system of technological plant units: a metal (molybdenum) plate heated by the RF field of the inductor between the base of the container-well and the pedestal preheats the hydrogen flow in the direction from the lower ring to the upper ring, chemically activating his. The base of the container-well is an endless source of carbon, in the through channels of which hydrocarbons are formed through the reaction of carbon with hydrogen at temperatures up to 1200°C, i.e. chemical gas transport of the initial reagent is carried out from the first zone to the second zone with Si substrates. At temperature 1360–1380°C in the second zone a reverse reaction occurs on the surface of the silicon substrates: decomposition of hydrocarbons with the formation of a silicon carbide compound on the surface of the silicon substrates along the entire height of the substrate holder assembly. The flows of gas and cooling water along the height of the HTCVD reactor preferably have the opposite direction. In this experiment, the level number is counted from top to bottom.

3. Study of the elemental composition of silicon carbide films by X-ray diffraction analysis

Qualitative X-ray diffraction analysis of the surface was carried out by taking rotational X-ray patterns in RKV-86 chamber and diffraction patterns on DRON-2 diffractometer using $\mathrm{CoK}_{\alpha\beta}$-radiation. For rotation chambers strips 2 mm wide were cut from wafers with a silicon carbide film, which were installed in the goniometric chamber holder. Round and slit beam collimators were used. A round collimator illuminated the area of the wafer up to 2 mm high, a slit collimator — maximum 1 mm high. X-ray patterns of rotation were interpreted according to the standard method using the Polanyi formula (1), where y and x — coordinates of the diffraction reflex on the X-ray pattern, D_k — effective chamber diameter, θ — Bragg angle related through the wavelength of X-ray quanta λ and an integer n with the interplanar distance d for a family of planes in reflective position by the Wulff–Bragg equation (2). No correction was made to the effective diameter of the chamber taking into account the final dimensions of the sample.

$$cos 2\theta = \cos\left(\operatorname{arctg}\frac{2y}{D_k}\right)\cos\frac{2x}{D_k}, \qquad (1)$$

$$2d\sin\theta = n\lambda. \qquad (2)$$

4. Study of silicon carbide films by Raman scattering method

Analysis of the spectral characteristics of the analyzed colloidal medium was carried out on experimental test rig consisting of a spectrometric system (RamanLife RL785, FOTON-BIO LLC, Russia) based on CCD detector and microscope (ADF U300, ADF, China). The spectra were excited using a laser module with a central wavelength of 532 nm. 50x LMPlan lens was used to focus the radiation onto the sample and to collect the scattered radiation. The diameter of the laser spot in focus was 5 mkm. Spectra were recorded in the spectral range 0–2000 cm^{-1} with spectral resolution 6–8 cm^{-1}. The limit of the permissible relative root-mean square deviation of wave number measurements is maximum 1%. The spectrometric system used is characterized by the absence of external cooling. The laser power was 20 mV for the surface-enhanced Raman-scattering spectroscopy method. The exposure time was 5 sec with 5 times averaging. Spectra are recorded using the EnSpectr program. Just before recording the spectral characteristics of the sample under study, the surrounding background signal was preliminary recorded. After this, the background component was automatically subtracted from the subsequent recorded spectra of the sample.

5. Analysis of spectra of silicon carbide films

Reflexes from the single-crystalline substrate were observed in all samples studied. This is silicon with a cubic diamond-type lattice (space group Fd3m with lattice constant $a = 5.4337$ Å) with wafer orientation perpendicular to the crystallographic directions $\langle 111\rangle$ and $\langle 100\rangle$.

On some samples with the $\langle 111\rangle$ orientation weak reflexes of the cubic modification of silicon carbide 3C–SiC were detected. Two recorded types of such reflexes can be noted.

1. Reflexes on fragments of Debye rings (Figure 1). This fact may indicate the predominantly polycrystalline nature of the silicon carbide film formed on single-crystalline silicon, the film, however, contains single-crystalline 3C-SiC inclusions.

2. Reflexes in the form of fragments of Debye rings (Figure 1). This may indicate a preferential orientation of fine grains of the silicon carbide film. In the above Figure, a fragment of the Debye ring is present at the equator of the X-ray pattern of rotation, i.e., in the direction of the reciprocal lattice vector $\langle 111\rangle$ of silicon single crystal or, at least, on the layer line of the X-ray pattern formed by the reciprocal lattice vectors $\langle 111\rangle$. This may indicate that the growing silicon carbide film inherits the crystallographic orientation of the single-crystal substrate.

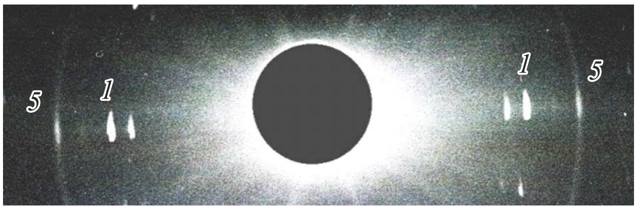

Figure 1. Reflex $\langle 111\rangle$ of single-crystal substrate (*1*) and fragment of Debye ring with a preferential orientation of silicon carbide (*5*).

In photographs from some samples with the single-crystal substrate orientation $\langle 100\rangle$, a system of Debye rings was detected, sometimes blurry, sometimes quite clear. Samples with a clear ring system were further examined using X-ray diffractometer. As a result, it was possible to obtain a larger number of diffraction lines (up to nine on the diffraction pattern versus seven on the X-ray pattern of rotation) and increase the accuracy of identifying interplanar spacings. All these lines are identified as belonging to the cubic modification of silicon carbide ($4\bar{3}m$). Fragments of the diffraction pattern (Figure 2) indicate the high perfection of the silicon carbide polycrystal.

On silicon wafers with the orientation $\langle 100\rangle$, a polycrystalline film of cubic modification of silicon carbide is formed without signs of preferential orientation.

On silicon wafers with the orientation $\langle 111\rangle$ a polycrystalline film of cubic modification of silicon carbide is formed with signs of inheritance of the orientation of the substrate and (or) containing single-crystal inclusions.

These results are also confirmed by Raman scattering spectra on silicon wafers grown at different levels of the substrate holder (Figure 3). The intensity of the peaks can be used to judge the thickness of the resulting silicon carbide film. In the region of optical vibrations 750–1050 cm^{-1} the spectrum of the films studied contains two groups of overlapping lines. The group of lines in the region 750–800 cm^{-1} is well described by the sum of TO mode spectra for 3C polytype. Also in the paper [8] it is shown that similar peak 795 cm^{-1} can accompany a line of the cubic polytype in material with structural defects. The weakly expressed line at 970 cm^{-1} corresponds to LO vibrations in 3C polytypes. Besides, carbon lines are also observed (1300 and 1700 cm^{-1}). According to the source [9] these lines correspond to D, G lines of carbon nanotubes.

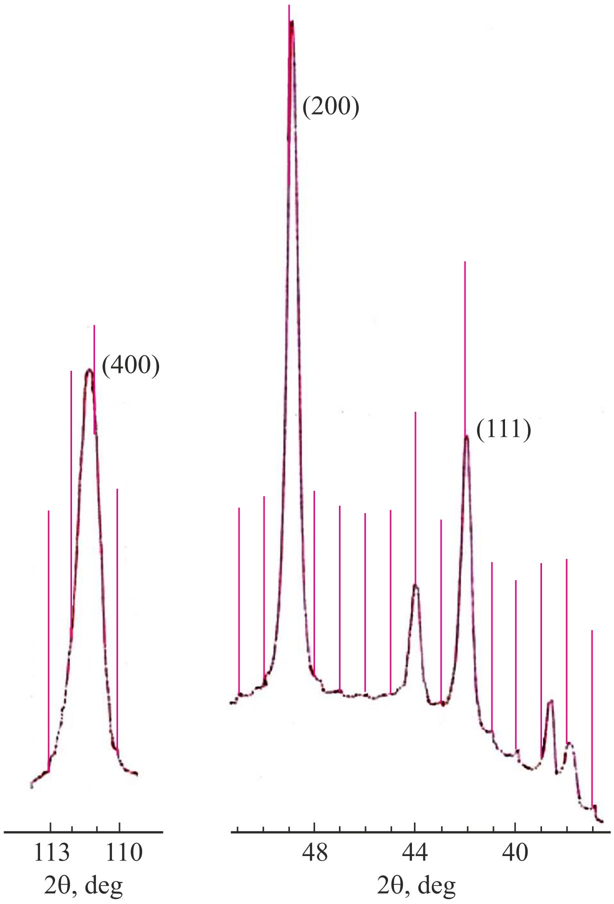

Figure 2. Fragments of diffraction pattern with the most intense diffraction lines of polycrystalline silicon carbide film.

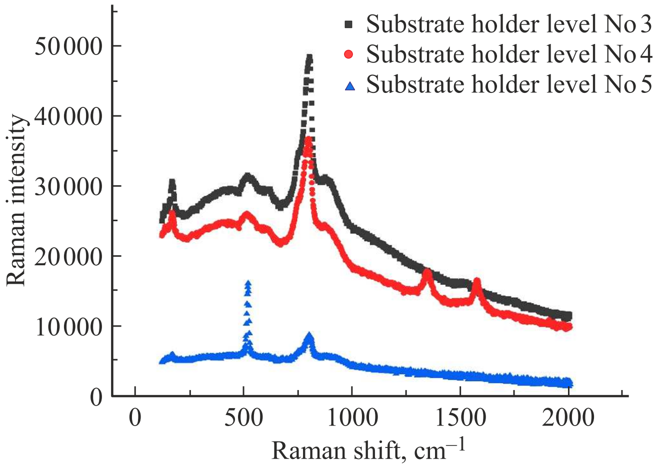

Figure 3. RSS spectra of film obtained by high-temperature chemical vapor deposition (substrate holder levels № 3–5).

The carbon presence on the surface of silicon carbide films can be explained by imperfect technology. When the anode current supply to the inductor is turned off, the substrate holder cools unevenly: at the top and bottom faster than in the middle. This leads to the fact that when deposited on cooled silicon substrate the carbon is not incorporated into the crystal structure.

6. Conclusion

Thus, as a result of HTCVD process a homogeneous polycrystalline silicon carbide film is formed. In some cases, carbon inclusions may be observed in it, which is explained by the presence of errors in the technological process.

Conflict of interest

The authors declare that they have no conflict of interest.

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