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Theoretical and Experimental Investigation of SiC Thin Films Surface

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Abstract:

This study describes morphology and structure of SiC thin films which are grown up by sublimation epitaxy in vacuum on the 6H-SiC substrates with thickness from tens of nanometers up to units of micrometers. Fashioned films are quite uniform in surface and volume. The crystal properties of the wafers and epitaxial layers are studied by electron diffraction investigation, X-ray techniques, and scanning probe microscopy. X-ray rocking curves show that structural perfection of SiC films is comparable with the structural perfection of monocrystalline 6H-SiC substrates. Calculated lattice parameters of epilayer by X-ray diffractometry also match with known values for 6H-SiC. Electron-diffraction measurement gives the confirmation of the crystallinity of the obtained layers and it is also proved by scanning probe microscopy. This technology allows making of defect treatment of the wafer in dependence on epitaxial conditions. Fundamental analysis in this field allows optimize conditions of thin films formation with prescribed properties and hence the using of them in the technology for elements of electronic engineering and by this reason the surface of monocrystalline SiC was analyzed.

INTRODUCTION

Using of the nonequilibrium processes for formation of thin films coatings with both disordered structure and micro- and nanostructure is one of the perspective directions in the development of new production technologies of electronic devices materials which hold much promise for information and energy transformation devices.

Striking examples of such materials are thin films coatings on the basis of amorphous and crystalline silicon, silicon carbide and solid solutions on the basis of SiC with metals nitrides with different amount of doping [1]. Silicon carbide are of interest in view of application possibilities in high-temperature, high-power, and high-frequency and optoelectronic devices [2], [3], structural component in fusion reactors, cladding material for gas-cooled fission reactors, and an inert matrix for the transmutation of Pu [4], catalyst support, high irradiation environments [5].

Development and modernization of devices which are based on thin films materials from memory discs up to photoelements and light diodes [6], [7], X-ray lenses and diffuse lattices, engineering products with protective coating [8] called forth the intensive investigation of their features and atomic structure in dependence of formation conditions.

The use of classical semiconductor materials (Si, Ge, A^3B^5, A^2B^6) is not effective because of their low temperature, pressure and radiation resistance in view of an application field expansion of present-day microelectronic devices with stable parameters in extreme conditions.

Today, there is a large demand in active components on the basis of thin layers of wide band gap semiconductors, persistent thin-film coatings in industrial electronics. One of these materials is silicon carbide (SiC), which exists in about 250 crystalline forms [9]. It is widely used in high-temperature/high-voltage semiconductor electronics. Nevertheless a major problem for SiC commercialization has been the elimination of defects [10]: edge dislocations, screw dislocations (both hollow and closed core), triangular defects and basal plane dislocations. Therefore, a formation of coatings on the basis of SiC with high chemical inertness, radiation resistance, homogeneity, uniformity, durability, mechanical strength and good adhesion to range of material is of great interest at present days [11]. Fundamental analysis in this field allows optimize conditions of thin films formation with prescribed properties and hence the using of them in the technology for elements of electronic engineering.

Epilayer or epitaxial layer is a single crystal layer formed on top of a single crystal substrate. An epitaxial layer will typically have a different doping level and or type than the substrate upon which the epitaxial layer is formed. In some cases the epitaxial layer may be a completely different type of material than the substrate upon which it is grown. If the substrate and the epitaxial layer are both the same element or compound then the process is homoepitaxy and if the epitaxial layer and the substrate are different elements or compounds then the process if hetroepitaxy. It is well known that physicochemical surface properties of any solid depend on crystal-lattice orientation and sharply differ from bulk properties.

EXPERIMENTAL RESULTS

There are over 200 polytypes of SiC structure. The most frequently occurring are 6H, 4H, 15R and 3C polytypes (Fig.1) [12].

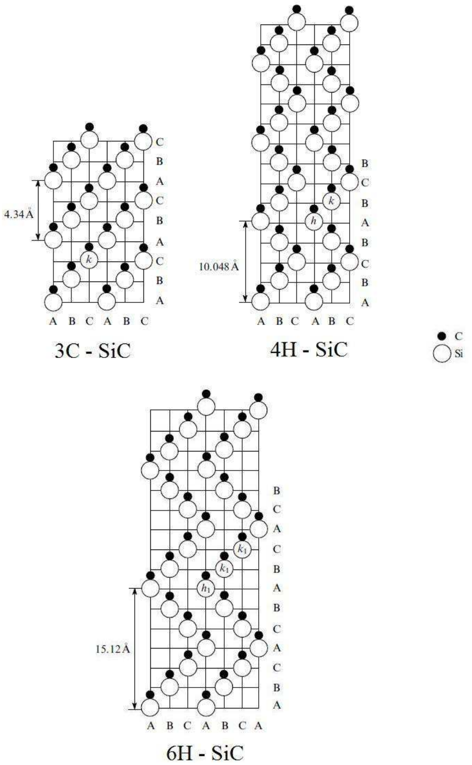

Fig. 1: Positions of Si and C atoms (open and full circles, respectively) in the (1120) plane for different SiC polytypes [12].

Composition of SiC polytype is defined by formation conditions, amount and type of impurities. Cubic polytype is more stable in comparison with hexagonal and the most unstable is 2H polytype [13]. By this reason we well describe direction [100] of diamond-like cubic crystal where every atom of a layer has two bonds with former and next layers. And it is possible to expect that every atom of atomically clean and smooth surface has two dangling bonds (Fig.2).

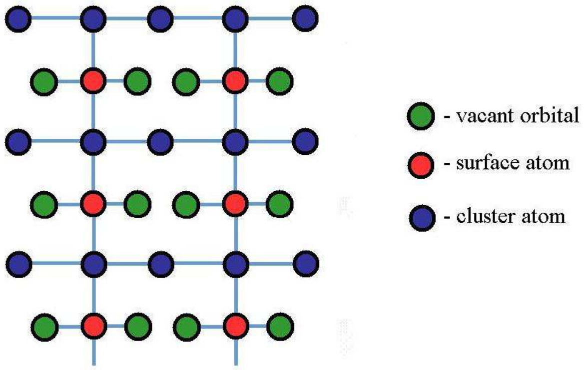

Fig. 2: Structure atomically clean and smooth surface.

But computer modeling shows that the minimum of potential energy responds to the structure in Fig.3.

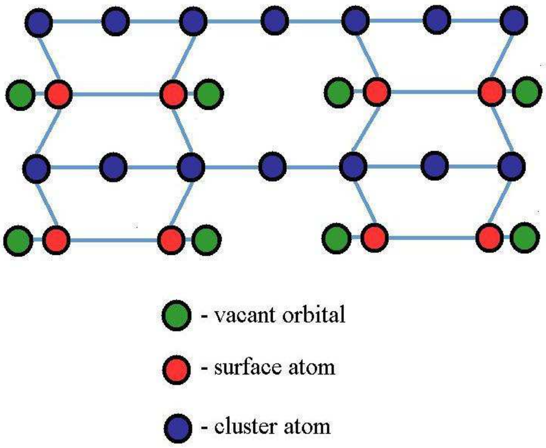

Fig. 3: Structure of surface with the minimum of potential energy.

The results are similar independently of choice of surface structure optimization and method of calculation. In all cases structure of cluster has the minimum of energy when surface structure differs from the plane structure.

Decreasing of potential energy caused by the reason that a part of surface atoms makes the intermediate bonds and reduces the amount of dangling bonds. Deformations of the valence angle of sp3 -hybridized orbitals of surface atoms will be equilibrated by released energy of chemical bond formation.

Surely the atomically clean and smooth surface is the abstraction and real surface always has the atoms of impurities of chemisorbed atoms and different defects. But according to the calculated results the reducing of concentration of intermediate bonds is not energy-optimal even in the case of hydrogen chemical adsorption.

In other words, the surface does not meet a demand of energy minimum if every atom has two bonds with hydrogen.

Quantum chemical analysis of activation energy for interaction process between two hydrogen atoms of two surface atoms shows that it is equal to 84 kJ/mol (Fig.4).

Hence, the most preferable surface structure corresponds to a condition when every surface atom has one intermediate bond with neighbor atom and another one with hydrogen.

Thus, surface structure of monocrystalline film differs from the plane structure which this surface should correspond to. Concentration of active center for chemical absorbtion is equal to the concentration of surface atoms. In case when the surface is saturated with hydrogen the chemical absorption mechanism should be considered as a process of hydrogen substitution.

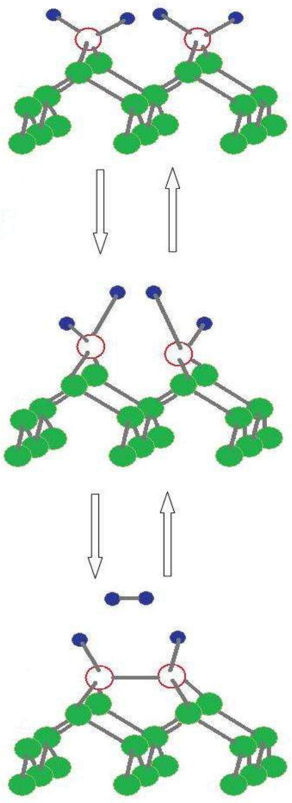

Fig. 4: Schematic figure of the interaction reaction between hydrogen atoms of two surface atoms.

High-temperature vacuum device was used for growing of SiC layers on the 6H-SiC substrate by sublimation sandwich method. This method allows obtain an epilayer - a region of epitaxially-grown material that forms a layer on the surface of a semiconductor body (Fig.5). A straight pipe of compact chemical clean graphite is used as heating spiral in the technological device. There is a multilayer shielding system of graphite tissue and felt for heating concentration and creation of defined temperature gradient around the heater.

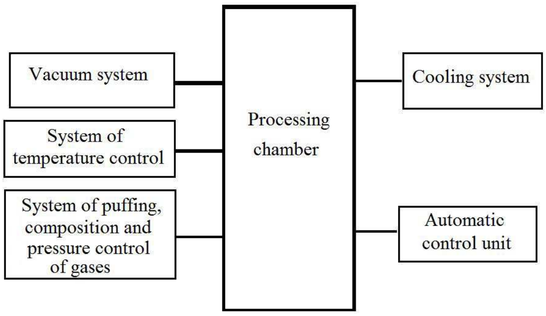

Fig. 5: Structure chart of high-temperature device for SiC growth by sublimation sandwich method.

Growth cell (crucible) is inside of storm proof graphite container which is inside a heater. The crucible material is zirconium carbide. It allows obtain the layers with predictable stoichiometry and high structural perfection.

Silicon carbide plates of 6H polytypic having n-type conductivity and containing uncontrolled impurities $N_d\text{-}N_a = 6\cdot 10^{17} \div 3\cdot 10^{18}\ \text{cm}^{-3}$ were used as substrates.

Schematic image of the hexagonal and crystal lattices of SiC is shown in Fig. 6. [12]

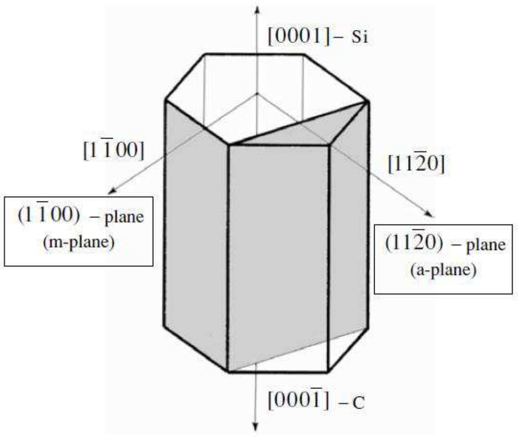

Fig. 6: Schematic image of the hexagonal and crystal lattices [12], [14].

The cleaning and preparation of substrate surface has been considered as main characteristic steps of fabrication. In order to remove defective layers after grinding and polishing, the substrates were chemically etched in the KOH at 750 K during 20 min. Then they were washed many times in distilled water in order to remove residuum of KOH. Right before a process the substrates were washed in ethanol and dried.

The plate of 6H-SiC monocrystal was studied by scanning tunneling microscopy with measurement head ST020NTF (NT-MDT) with range of current ±100 pA. The result of interatomic spacing is corresponding to the theory [14]. But such order of grown crystals is not typical on large areas because of influence of growth processes which forms a large amount of different types of surface imperfections.

Films of SiC had the thickness from tens of nanometers up to units of micrometers and for fast tests the Linnik interferometer MII-4 was used which allows defining the thickness of layers by shift of interference fringes connected with reflection from upper and bottom plates with max.10% errors.

Diffraction pattern of the SiC film is be characterized by two pronounced peaks (doublet $K_{\alpha 1}$ and $K_{\alpha 2}$) at $2\theta = 133.3^{\circ}$ and 133.9° angles. Their appearance is connected with the fact that even after filtering the CuK_{α} radiation is not monochromatic. There are two wavelengths $\lambda_{\alpha 1} = 1.54051$ Å and $\lambda_{\alpha 2} = 1.54433$ Å in radiation and generally at large angles doublet $K_{\alpha 1}$ and $K_{\alpha 2}$ is registered (at sufficient resolution of the spectrograph). Parameters calculated by this diffraction pattern are c = 15.1164 Å and a = 3.083 Å and matched with known parameters for 6H-SiC

(Fig.7). In order to study structural perfection, the X-ray rocking curves were measured from substrates and epitaxial film. The spectra slightly differ. This means that perfection of obtained films and substrates is almost similar.

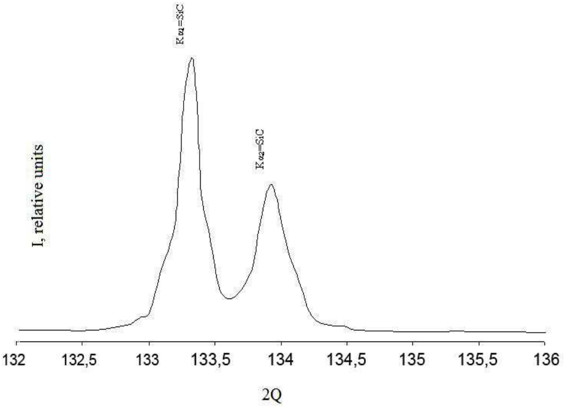

Fig. 7: Diffraction X-rays on SiC film.

Structural features were measured by diffraction fast electrons and the point electron diffraction patterns confirm the monocrystallinity of the films.

The atomic-force microscopy also confirms the monocrystalline structure of the films. But in some places the micropores have been observed. These micropores are caused by imperfection of the substrate (Fig. 9), but the micropores have disposition to overgrowing with growth of film thickness (Figs. 9).

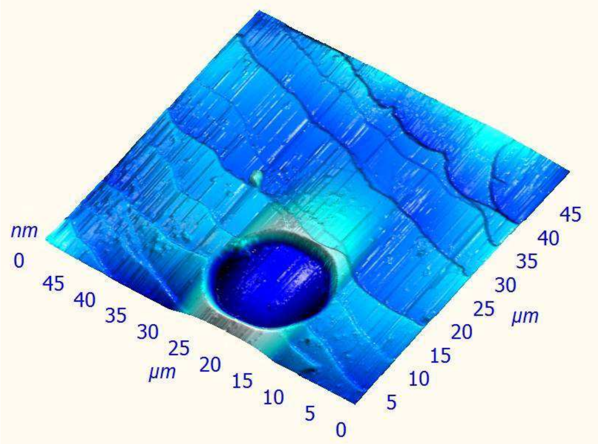

Fig. 8: Micropore of SiC film with depth 293 nm.

On the basis of Figs. 4 the tolerance of polishing (0°24.06′) has been calculated, which shows the deviation of the processed wafer from the crystallographic direction (0001).

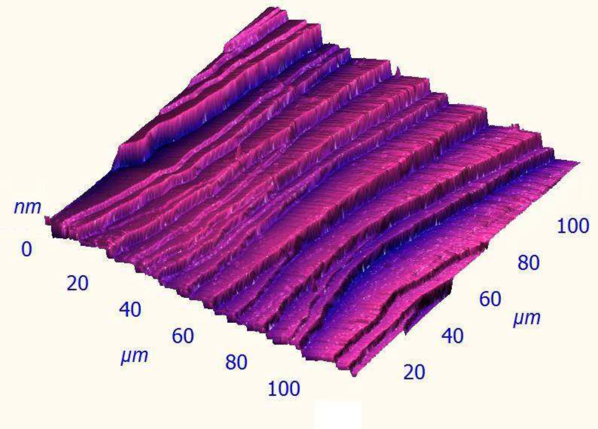

Fig. 9: AFM-image of SiC film (scan size 120x120 μm). Average roughness = 81,4107 nm.

CONCLUSION

Thin films of silicon carbide were grown by sublimation epitaxy in vacuum on the 6H-SiC substrates. Structural properties of the initial substrates and the epilayers were studied by both electron-diffraction and X-ray diffraction methods. Electron-diffraction measurement gives the confirmation of the crystallinity of obtained layers. Experimental results show that a lattice perfection of epilayer is equal to that of monocrystalline substrate. These results are also validated by scanning probe microscopy. So, this technology of fabrication of SiC thin films allows carry out a treatment of initial substrate defects in dependence of the process conditions. The processes of nucleation and the behavior of monocrystalline SiC surface with cubic structure were also studied.

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