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The formation of SiC films by magnetron sputtering

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This paper is devoted to the synthesis of solid silicon carbide (SiC_x) films on the surface of single-crystal silicon (c-Si) with a thin interlayer of amorphous silicon (a-Si) by magnetron sputtering as well as to establish new regularities in the influence of heat treatment on composition, crystallization processes and structure of layers. A principal difference between the method of synthesis and the traditionally used magnetron sputtering is the 13.56 MHz high-frequency magnetron sputtering of a silicon target and a graphite target. An amorphous $SiC_{0.97}$ film with a density of 3.179 g/cm^3 and 165 nm thick was obtained under the deposition regime: rf = 150 W, 13.56 MHz; Ar – 2.4 l/h, 0.4 Pa; 100°C, 2400 s; containing SiC nanocrystals after annealing (1100°C, 30 min, Ar). Synthesis of an amorphous SiC_x film with a density of 3.204 g/cm^3 at a long sputtering of Si and C targets – 14400 s, containing nanoclusters with a predominance of truncated SiC bonds, was carried out.

Key words: silicon, semiconductors, silicon carbide, crystallization, magnetron sputtering
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1 Introduction

Important physical and chemical properties of silicon carbide for semiconductor electronics, such as wide bandgap (Eg = 2.3–3.5 eV), high melting point (2830°C), high chemical resistance and thermal conductivity, high carrier mobility and hardness (33400 Mn/m^2) caused its wide application in radiation-resistant electronics, high-temperature electronics, high-frequency electronics, optoelectronics [1-3]. Silicon carbide is also widely used as heat-resistant materials in the manufacture of rifled discs and drills, in the design of thermonuclear reactors, in composition heat-resistant materials, in coatings of the hull of spacecrafts [4]. Electronic devices based on SiC have a high speed and the ability to work at temperatures up to 600 °C [5, 6].

Unfortunately, since it is still difficult to grow SiC material of crystalline quality to meet requirements for a large scale industrial application, small-size and high-cost SiC wafers severely limit their applications at present [7]. The difference in the lattice parameters of the silicon carbide and monocrystalline silicon is ~20%, and the difference in their thermal expansion coefficients is ~8%. Therefore, the growth of epitaxial SiC layers on a Si substrate is a nontrivial problem [8, 9]. For example, by means of ion implantation [2, 5-8, 11, 12], ion-beam sputtering [13-15] or plasma enhanced chemical vapor deposition [8, 16] it is possible to obtain amorphous SiC films with subsequent crystallization during annealing (900-1300°C). Successes were achieved in the synthesis of thin epitaxial SiC films on Si by the substitution of atoms [9, 10, 17-19]. The method of magnetron sputtering has become widespread due to relatively high growth rates, good adhesion of SiC films and sufficiently low cost of the technological process [20-23]. In [20] magnetron sputtering of a two-component target, which is composed of separate parts of C and Si, is proposed. In general, at temperatures below 500 °C, the structure of SiC films is amorphous. In magnetron sputtering with direct current, polycrystalline fused targets of silicon and carbon are commonly used [21]. An alternative to using a fused target is sputtering a pure silicon target in a mixture of argon and

methane [22]. The resulting SiC films had a polycrystalline structure with nanometer-sized columnar grains. In [23], a method was proposed for depositing amorphous a-$Si_{1-x}C_x$ by means of radio-frequency magnetron sputtering of two or more targets.

In this work, the silicon carbide films on the surface of a thin layer of amorphous silicon grown on the surface of a single-crystal silicon substrate were synthesized by means of magnetron sputtering.

2 Materials and methods

The deposition of SiC films was carried out on the MAGNA TM-200-01 unit with the simultaneous sputtering of the silicon target and the graphite target in the high-frequency regime of 13.56 MHz at a power of 150 W. The gas Ar flow rate was 2.4 l/h, the chamber pressure – 0.4 Pa, the substrate temperature – 100°C, deposition time 2400 and 14400 s. Single-crystal silicon wafers of (100) orientation with dimensions 7×7×0.3 mm and resistivity 4-5 Ω·cm as substrates were used [11,12,13].

The composition and structure of the film after deposition and annealing at the temperature of 1100°C were investigated using IR spectrometer Nicolet iS-50 (Thermo Scientific, USA) [12,13].

Phase composition of the films was determined by highly sensitive X-ray diffraction using narrowly collimated (0.05 × 1.5 mm^2) CuK_α X-ray beam [11-13].

The density and thickness of the films had determined by X-ray reflectometry through registration of the angular dependence of the reflection coefficient using two spectral lines CuK_α (0.154 nm) and CuK_β (0.139 nm) on the installation Complexray C6 [12, 13, 24].

3 Results and discussion

The deposited films were investigated by X-ray reflectometry using two spectral lines CuK_α and CuK_β. According to the value of the critical angle of the total external reflection $2\theta_c$ = 0.51994° (Table 1, Figure 1b), the SiC_x film density was determined using the Henke program [25], which was 3.179 g/cm^3 and corresponds to the density of $SiC_{0.97}$ layer. The composition of the SiC_x layers can be determined approximately from the expression [12]:

$$x = x_1 + (\rho_x - \rho_1)\bullet(x_2 - x_1)/(\rho_2 - \rho_1), \quad (1)$$

where x_2 = 1, x_1 = 0, ρ_2 = 3.21 g/cm^3, ρ_1 = 2.33 g/cm^3, ρ_x = 3.179 g/cm^3, $x = N_C/N_{Si}$ = 0.965 and the density of the SiC_x layer is an intermediate value between the density of SiC (or Si_1C_1) and Si (or Si_1C_0). According to the formula $SiC_x = Si_{1-x/(1+x)}C_{x/(1+x)}$, the density corresponds to the composition $SiC_{0.965} = Si_{51}C_{49}$. The film thickness was about 166 nm (Table 2, Figure 1a).

Table 1 – Determination of the layer density ρ using the Henke program

Film	I_{max}, s^{-1}	$I_{max}/2$, s^{-1}	$2\theta_c$, degree	θ_c, degree	θ_c, mrad	ρ, g/cm^3
SiC_x	708339	354170	0,51994	0,25997	4,537	3,179

Table 2 – Determination of the layer thickness d by the formula 2d·sinθ = λ, or d = λ/2θ

Film	$(2\theta)_j$, degree	$(2\theta)_i$, Degree	j – i	$2\theta_{av}=[(2\theta)_j - (2\theta)_i]/(j-i)]$, degree	λ, nm	d, nm
SiC_x	1,806	0,740	20	0,0533	0,15420	165,8
SiC_x	1,666	0,704	20	0,0481	0,13923	165,8

After annealing at the temperature of 1100°C for 30 minutes in Ar atmosphere, the density decreases up to 2.792 g/cm^3 (Table 3) and the layer thickness increases up to 174 nm (Table 4). The change in the film density and its composition to $SiC_{0.525} = Si_{66}C_{34}$ after annealing assumes that under the action of a high-frequency plasma of 13.56 MHz a structural phase of high density was precipitated, which decays after annealing.

In IR spectra, the presence of a wide SiC peak in the range 700-1030 cm-1 and SiO2 peak at 1100 cm^{-1} before and after annealing (Figure 2).

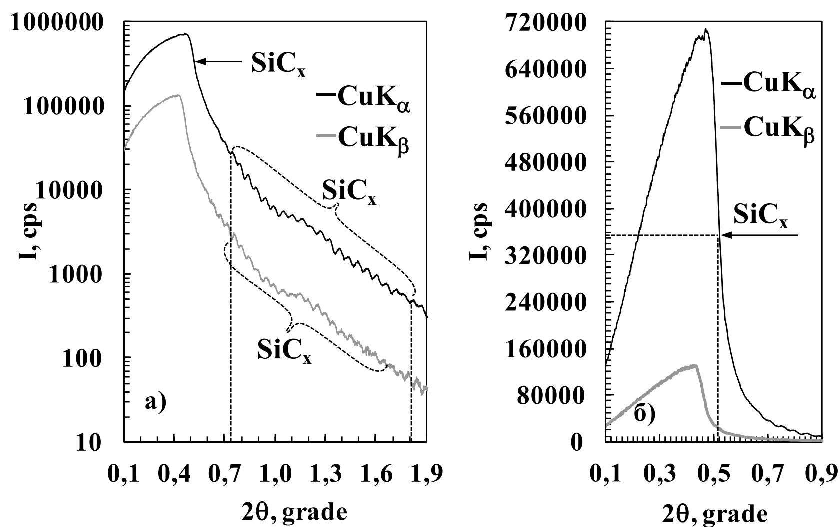

Figure 1 – X-ray reflectometry using two spectral lines of CuK_α (0.154 nm) and CuK_β (0.139 nm) of the SiC_x film synthesized on the surface of Si substrate by magnetron sputtering (150 W – rf, 2400 s, Ar – 2.4 l/h, 0.4 Pa , 100°C), in logarithmic (a) and natural (b) scales

Table 3 – Determination of the layer density ρ using the Henke program

Film	I_{max}, s^{-1}	$I_{max}/2$, s^{-1}	$2\theta_c$, degree	θ_c, degree	θ_c, mrad	ρ, g/cm^3
SiC_x	352693	176347	0,48730	0,24365	4,2525	2,792

Table 4 – Determination of the layer thickness d by the formula $2d \cdot \sin\theta = \lambda$, or $d = \lambda/2\theta$

Film	$(2\theta)_j$, degree	$(2\theta)_i$, Degree	j – i	$2\theta_{av}=[(2\theta)_j - (2\theta)_i]/(j-i)]$, degree	λ, nm	d, nm
SiC_x	1,834	0,820	20	0,0507	0,15420	174,3
SiC_x	1,706	0,748	21	0,04562	0,13923	174,9

The appearance of SiC(111) line of polycrystalline silicon carbide phase on the X-ray diffraction pattern (Figure 3) after annealing (1100°C, 30 min, Ar) was observed. The absence of SiO_2 lines indicates the absence of thick SiO_2 amorphous layer or SiO_2 crystallites. As a result, the SiO_2 peak of IR absorption corresponds to the natural oxide on the back surface of c-Si. Thus, the formation of a SiC film after deposition by magnetron sputtering in the high-frequency regime and annealing at 1100°C for 30 minutes is reliably shown.

Long-term deposition of SiC_x thick films on the c-Si surface using the MAGNA TM-200-01 unit with simultaneous sputtering of targets of silicon and graphite in the high-frequency regime of 13.56 MHz was carried out with parameters as follows: the magnetron power was 150 W, argon gas flow was 2.4 l/h, the pressure in the chamber was 0.4 Pa, the substrate temperature was 100°C, the sputtering time was 14400 s. It is shown by X-ray reflectometry that the film density corresponding to the critical angle of total external reflection θ_c = 0.25648° was 3.204 g/cm^3 (Figure 4b, Table 5) and is practically equal to the density of silicon carbide 3.21 g/cm^3. No intensity oscillations are observed (Figure 4a) due to an increase in the sputtering time by a factor of 6 and a thickness of up to 1 μm in comparison with a duration of 2400 s and a thickness of 165.8 nm (Table 2). X-ray reflectometer determines the film thickness in the range of 2-400 nm.

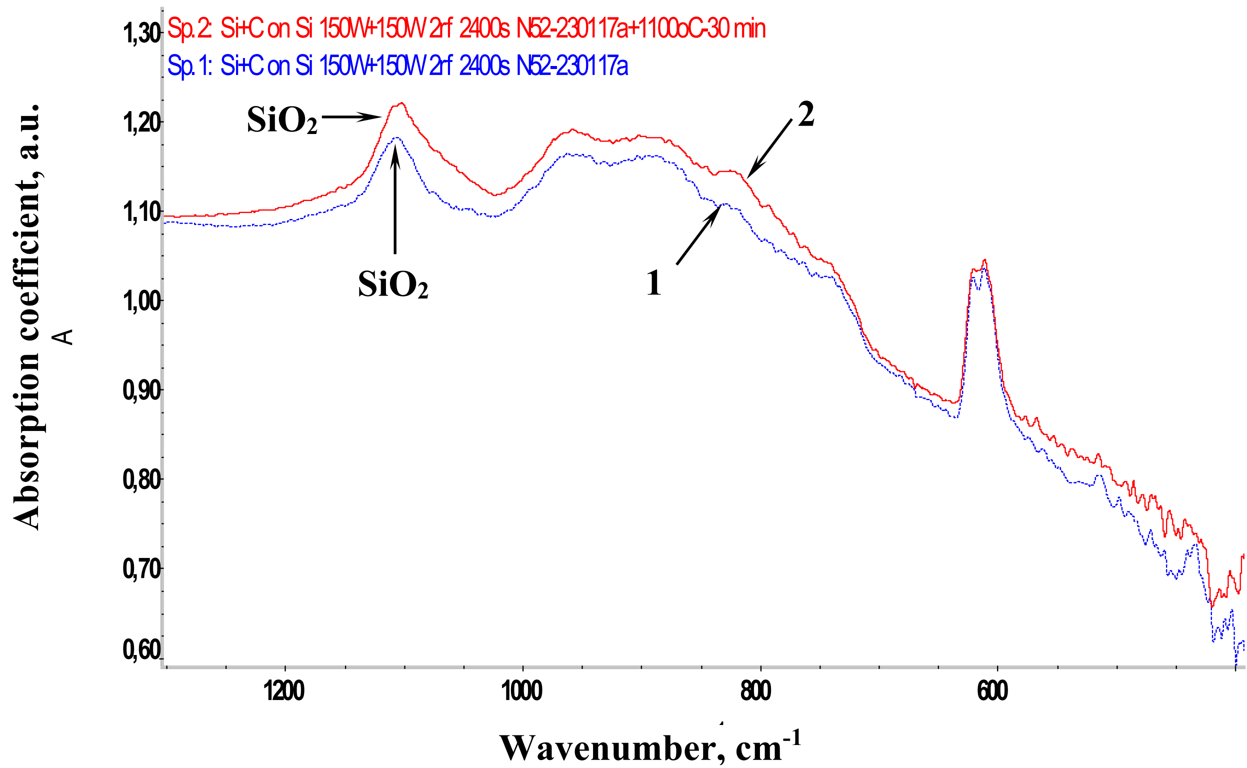

Figure 2 – IR absorption spectra of a SiC_x film synthesized on the surface of a Si wafer by magnetron sputtering (150 W, 2400 sec, Ar-2.4 L / h, 0.4 Pa): 1- after deposition, 2 – after annealing at 1100°C for 30 min (Ar)

Figure 3 – X-ray diffraction pattern of thin SiC_x film deposited by magnetron sputtering, after annealing at 1100°C for 30 min in an Ar atmosphere

In the IR spectrum of the film, a broad peak is observed in the region 440-1200 cm^{-1} with an amplitude of 0.220 a.u. and a half-width of 360 cm^{-1}, indicating the amorphous nature of the SiC film (Figure 5). Indeed, as shown in [12], for the ion-synthesized $SiC_{1.0}$ and $SiC_{1.4}$ layers, the half-width of the IR-transmission peak of the amorphous layer was 300 cm^{-1} with a maximum in the region of 700-795 cm^{-1}, i.e. below the value of 795.9 cm^{-1}, characteristic of tetrahedrally oriented Si-C bonds in β-SiC (or 799.5 cm^{-1} in 2H-SiC, 797.6 cm^{-1} in 4H-SiC, 797.0 cm^{-1} in 6H-SiC, 797.5 cm^{-1} in 15R-SiC). In Figure 5, a peak of SiO_2 with a maximum at 1100 cm^{-1} and an amplitude of 0.06 due to the presence of SiO_2 layer on the underside of the Si substrate, is also observed. A feature of the SiC peak is the location of the maximum in the 860 cm^{-1} region, suggesting the prevalence of truncated SiC bonds absorbing in the region above 795.9 cm^{-1}.

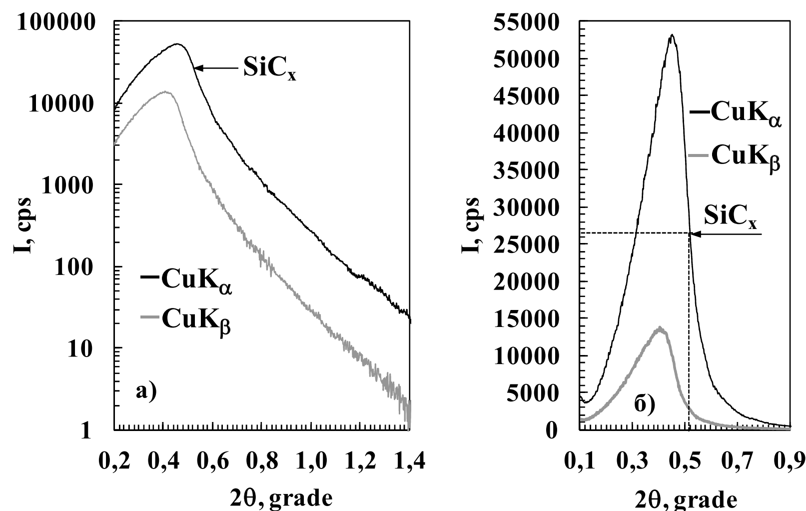

Figure 4 – X-ray reflectometry of a SiC_x film synthesized on the surface of a Si wafer by magnetron sputtering (150 W-rf, 14400 s, Ar-2.4 l/h, 0.4 Pa, 100°C), in logarithmic (a) and natural (b) scales

Table 5 – Determination of the layer density ρ using the Henke program

Film	I_{max}, c^{-1}	$I_{max}/2$, c^{-1}	$2\theta_c$, degree	θ_c, degree	θ_c, mrad	ρ, g/cm³
SiC_x	53212	26606	0,51295	0,25648	4,476	3,204

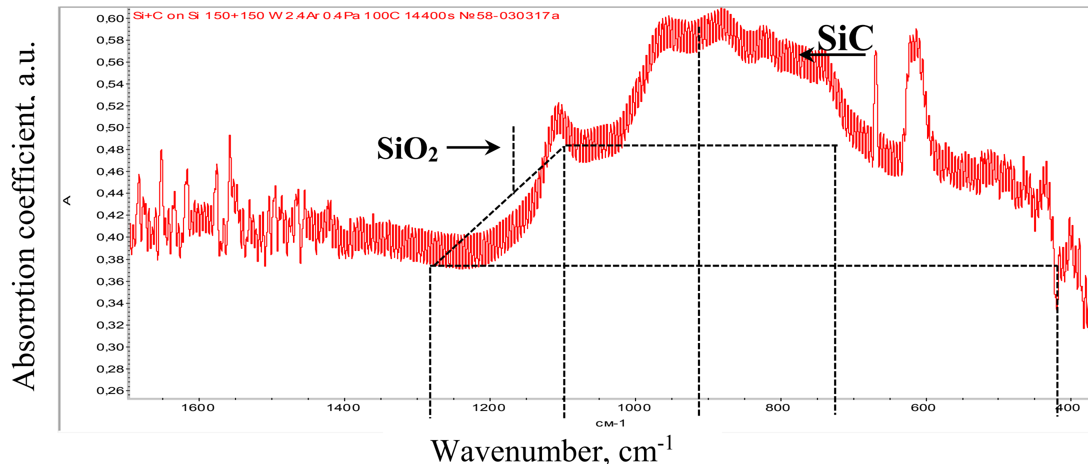

Figure 5 – IR absorption spectrum of a $SiC_{1.0}$ film deposited on the surface of a Si wafer by magnetron sputtering (150 W, 13,56 MHz, 14400 s, Ar-2.4 l/h, 0.4 Pa)

4 Conclusions

The synthesis of silicon carbide (SiCx) films on the surface of single-crystal silicon (c-Si) with a thin interlayer of amorphous silicon (a-Si) by magnetron sputtering. A principal difference between the method of synthesis and the traditionally used magnetron sputtering is the 13.56 MHz high-frequency magnetron sputtering of a silicon target and a graphite target. An amorphous $SiC_{0.97}$ film with a density of 3.179 g/cm³ and 165 nm thick was obtained under the deposition regime: rf = 150 W, 13.56 MHz; Ar – 2.4 l/h, 0.4 Pa; 100°C, 2400 s; containing SiC nanocrystals after annealing (1100°C, 30 min, Ar). Synthesis of an amorphous SiC_x film with a density of 3.204 g/cm³ at a long sputtering of Si and C targets – 14400 s, containing nanoclusters with a predominance of truncated SiC bonds, was carried out.

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