Functional Materials 14, No.2 (2007) © 2007 — Institute for Single Crystals

Structure and stress state of ion-plasma hafnium condensates

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Received April 2, 2007

The 0.05–0.5 μm thick films have been obtained from GFE-1 grade hafnium target by magnetron sputtering using argon ions. Purity of the obtained films was controlled by X-ray fluorescence spectroscopy. The structure of films was explored by X-ray diffractometry. The compression residual stresses in the α–Hf films and the values of crystal lattice periods have been determined by X-ray strain measurement.

Методом магнетронного распыления ионами аргона мишени из гафния марки ГФЭ-1 получены пленки толщиной 0,05–0,5 мкм на различных подложках. Чистота получаемых пленок контролировалась рентгеновской флуоресцентной спектроскопией. Структура пленок исследовалась рентгеновской дифрактометрией. Методом рентгеновской тензометрии в пленках α–Hf выявлены сжимающие остаточные напряжения и определены значения периодов кристаллической решетки.

One of the important application field of hafnium was the production of special alloys, particularly, refractory and high-melting ones, with hafnium either as the basic component or an alloying dope. The commercially pure hafnium was considered as a promising construction material for chemical engineering due to high chemical and thermal resistance. Moreover, the high-melting hafnium compounds (oxide, carbide, nitride, and fluoride) are of great interest for practical applications [1]. The nuclear pure hafnium has been successfully used as a neutron absorber in the control system for protection of the thermal neutron atomic reactors [2].

Hafnium belongs to rare and expensive materials with a complicated production technology, so it is reasonable to use thin enough hafnium based coatings upon less expensive construction materials. Usually, the coatings are prepared chemically, by decomposition of hafnium chloride compounds at 800–1000°C. Application of ion-plasma techniques for hafnium deposition could provide a substantially improved coating quality. In this case, the main advantages of the ion-plasma method are realized: high deposition rate, good adhesion to the substrate, enhanced condensate density, a possibility to form the high quality coatings at lower substrate temperatures [3]. The purpose of the work was to prepare the hafnium films and to study the structure, substructure, and stress state thereof.

For preparation of hafnium films of 0.05 to 0.5 μm thickness, the methods of ionic and magnetron sputtering of the hafnium target by argon ions were used. As the target material, hafnium (GFE-1 grade, 99.9 wt.% purity with impurity content of O_2 < 0.05 wt.%, Fe≈0.03–0.04 wt.%, and Zr = 0.2 wt.%) was used. At the target sputtering using an ion gun with a saddle-

shaped electrical field, the working gas pressure in the vacuum chamber was $5 \cdot 10^{-3}$ Pa, and the deposition rate did not exceed 0.006 nm/s. The magnetron sputtering was carried out under $(1-5) \cdot 10^{-1}$ Pa pressure and condensation rate (ω) 0.1–0.4 nm/s. To reduce the partial pressure of active gases in the vacuum chamber, an additional getter pump was used. The films were deposited onto substrates of fluorophlogopite (FP) mica, silicon and glass ceramics (GC) in the substrate temperature (T_s) range from 300 to 850 K. Prior to the film deposition, the substrates were preliminary heated at a higher temperature. The purity of the films was controlled by X-ray fluorescence spectroscopy using a SPRUT unit (Ukraine) in silver anode radiation. The film thickness was measured by an optical interferometer MII-4 and then calculated more precisely by the Hf–K_α characteristic line intensity in the X-ray fluorescence spectrum.

The film structure was studied by X-ray diffraction method. The measurements were carried out using a DRON-2 instrument in the filtered Cu–K_α radiation. The phase composition, texture, and substructure were investigated by usual analysis of intensity, positions, and profile shapes of the diffraction lines [4, 5]. The card-index of the International Centre for Diffraction Data was used to identify the diffraction pattern. The texture scattering angle was defined by "rocking curve" measurements. The coherence length and the micro-strain levels were calculated from the diffraction maxima broadening by approximation method. The Hall graphs were plotted for three (00l) reflection orders using Cauchy function to describe the diffraction line shape. The residual macro-stress in α–Hf films were measured by the special X-ray tensometry technique for hexagonal single-crystalline and high-textured samples [6, 7]. The oblique scans of five α–Hf reflections (213), (006), (205), (106) and (214) positioned in the precision angle range were done at the crystallographic angles ψ, and different tilt angles φ in the sample plane. The stress analysis is reduced to a multi-parameter dependence:

$$d_{hkl}(\varphi_{hkl},\psi_{hkl}) = \left(\frac{4}{3} \cdot \frac{h^2+k^2+hk}{a_0^2} + \frac{l^2}{c_0^2}\right)^{-\frac{1}{2}} \times \\ \times\left(1+S_1(\varphi_{hkl},\psi_{hkl})\sigma_1 + S_2(\varphi_{hkl},\psi_{hkl})\sigma_2 + \\ + S_3(\varphi_{hkl},\psi_{hkl})\sigma_3\right)$$

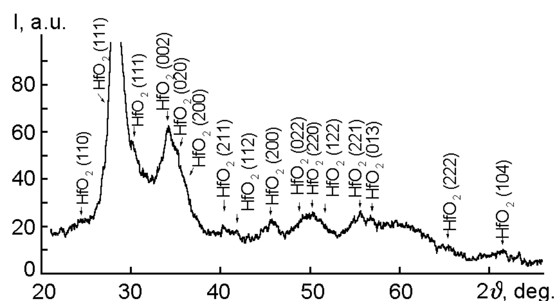

Fig. 1. The diffraction pattern obtained in Cu–K_α radiation for the HfO_2/FP film prepared by ion-sputtering of hafnium target.

where:

$$S_1(\varphi_{hkl},\psi_{hkl}) = \\ = \sin^2\psi_{hkl}\left(\cos^2\varphi_{hkl}(s_{11} - s_{12}) + s_{12} - s_{13}\right) + s_{13};$$

$$S_2(\varphi_{hkl},\psi_{hkl}) = \\ = \sin^2\psi_{hkl}\left(\cos^2\varphi_{hkl}(s_{12} - s_{11}) + s_{11} - s_{13}\right) + s_{13};$$

$$S_3(\varphi_{hkl},\psi_{hkl}) = \sin^2\psi_{hkl}(s_{13} - s_{33}) + s_{33},$$

where d_{hkl} is interplanar distance for the (hkl) reflection measured in the direction specified by φ and ψ angles; a_o, c_o, the lattice parameters for the non-strained crystal; σ_1, σ_2, σ_3, the major components of the stress tensor; s_{11}, s_{12}, s_{13}, s_{33}, the coefficients of the crystal elastic compliance. In the case of asymmetric biaxial stress state ($\sigma_3 = 0$), the technique provides the independent determination of the residual stresses σ_1 and σ_2, and the lattice parameters a_o and c_o, corresponding to the non-strained state. The calculations were performed using the special software for the Hook-Geeves optimization. In the calculations, the elastic compliance coefficients for α–Hf were taken from [8]. The treatment of the experimental diffraction profiles were performed using the original software "New profile".

The phase analysis has shown the formation of hafnium oxide with orthorhombic lattice in the films of 0.1 μm thickness deposited using ion-sputtering method at T_s = 300 K independent of the substrate type. A typical diffraction pattern is presented in Fig. 1. The HfO_2 lines are broad and low-intense. This indicates the oxide films being nano-structured with crystallite size about 6 nm. Oxygen saturation of the films is caused by hafnium high reactivity, apparently through oxygen chemisorption at

the growing film surface or as a result of reaction within the chamber. High oxygen content is due to both a low deposition rate and the absence of the working gas additional cleaning.

The quality of the films prepared using magnetron sputtering was defined mainly by the substrate material. The continuous smooth films were formed on the silicon and glass ceramic (GC) surfaces. The films deposited onto fluorophlogopite mica were flaked partially forming bubbles, cracked, and fell. However, the film phase composition was the same, independent of the surface quality. The lines of α–Hf with hexagonal close-packed crystal lattice were revealed in the diffraction patterns of all the magnetron-sputtered films studied. The lines of HfO_2 oxide were absent. Hence, the additional working gas cleaning at the magnetron sputtering suppresses the oxide formation.

In Fig. 2, a diffraction pattern for the film deposited onto the silicon substrate at 830 K is shown as a typical one of all the magnetron-sputtered films studied. The intensity ratio of α–Hf lines differs considerably from the ratios characteristic for polycrystalline hafnium with random crystallite orientation. The intensity of (002) and (004) reflections is substantially higher than of other lines revealed: (100), (101), and (200). The (002) reflection rocking curve width does not exceed 15 deg for all the films. Rotation of the samples about the normal to the film surface causes no intensity variations both for the reflections from crystallographic planes parallel to the surface and from oblique ones. This indicates the presence of axial type texture with [001] axis normal to the film surface.

The oblique diffraction measurements in the α–Hf films reveal the residual compressive stresses, and the crystal lattice parameters a_o and c_o for non-stressed section were determined. The residual stresses in the films have been found to be symmetrical $\sigma_1 = \sigma_2$ with values of −200 and −900 MPa on the silicon and glass ceramic substrates, respectively. Note that the stresses due to the thermal expansion coefficient difference between the film and the substrate are estimated to be tensile stresses of values +190 and +40 MPa, respectively. It can be concluded that it is just the so-called "structure stresses" that contribute mainly to the film stress state [9]. One of possible reasons for the stress arising may be the structure densification due to point defect accumula-

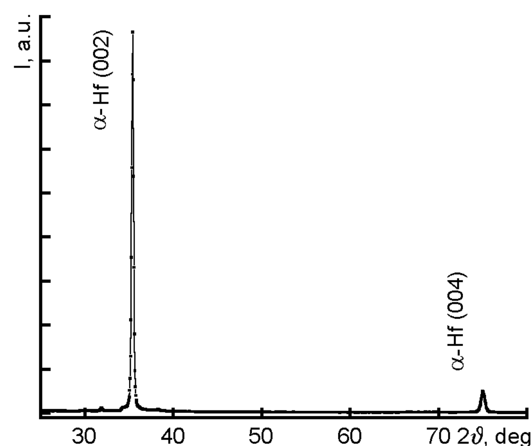

Fig. 2. The diffraction pattern obtained in Cu–K_α radiation for the α–Hf/Si film deposited by magnetron sputtering of hafnium target.

tion and redistribution followed by formation of dislocation loops. The lattice parameters calculated for the hafnium films: $a_o = 0.31965$ nm, $c_o = 0.50576$ nm for Hf/Si system, and $a_o = 0.31964$ nm, $c_o = 0.50593$ nm for Hf/GC, exceed the reference parameters for the bulk pure hafnium ($a_n = 0.31952$ nm and $c_n = 0.50569$ nm [4]). As the Hf/GC films were deposited at lower rates than Hf/Si ones, a comparative analysis of the results allows the following conclusion. During the growth, the condensate captures the vacuum chamber residual oxygen, but its quantity is too low to form an oxide, so, a solid solution is formed in a concentration that increases as the deposition rate decreases. According to estimations, the lattice parameters obtained have been estimated to correspond to the dissolved oxygen concentration ≤1 at.%.

As the substrate temperature rises from 300 to 820 K, and the film thickness increases from 0.06 до 0.2 μm, the Bragg reflections become narrower (by a factor of 1.5 to 3) indicating the perfection degree increase in the films. So, the coherent length region size (CLR) estimated from the (002) reflection using Selyakov-Scherrer equation shows the increase from 30 up to 90 nm. The refinement of CLR using approximation method taking into consideration the micro-strain contribution has shown that the diffraction line broadening could not be explained only by the two factors — micro-strains and CLR. The Hall plots presented in Fig. 3 pass to the negative part of the ordinate axis. This behavior is possible, if there are dislocation loops in the sample, which make another source of

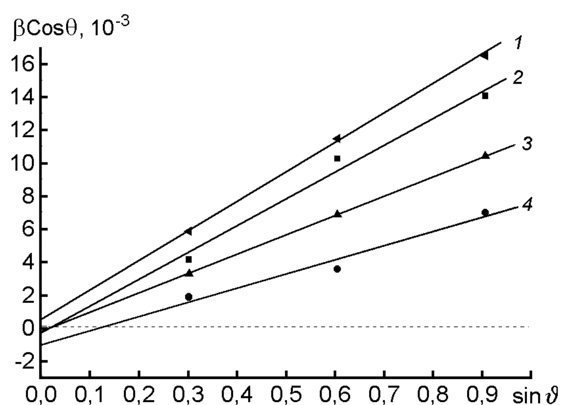

Fig. 3. The Hall graphs plotted using α–Hf (002), (004), (006) reflections for the samples prepared under different deposition conditions: *1* — T_s = 850 K, ω = 0.1 nm/s; *2* — T_s = 300 K, ω = 0.25 nm/s; *3* — T_s = 720 K, ω = 0.27 nm/s; *4* — T_s = 820 K, ω = 0.37 nm/s.

long-range fields displacing the atoms out of the crystal lattice sites and contributing additionally to the diffraction line broadening. For the crystals highly distorted both by packing defects and dislocation loops, the diffraction peaks weaken, broaden, and shift the more, the larger are the diffraction vectors thereof [10]. Note that for polycrystalline annealed α–Hf, the reflection intensity ratio of (002), (004), and (006) is approximately 100:7:3. For the samples studied (Fig. 3), the experimental intensity ratio indicates weakening the high order peaks. So, for the sample No.3, this is already 100:5:1; for No.2, 100:2:<1; for No.1, the second order peak is weakened by a factor of 4, while the third order one being almost invisible. The revealed features support the hypothesis about the dislocation loop formation.

Thus, the analysis of diffraction maxima positions, intensities, and width indicates that the bombardment of the growing film results in the condensate densification and formation of high compressive stress due to formation of the secondary interstitial type condensation defects [9, 11]. Those stresses may be partially compensated by the internal stresses of thermal nature. For the films deposited onto the substrates of the synthetic mica, fluorophlogopite, the thermal stresses are compressive. The addition of "structural" stresses to the thermal ones results in overcoming film-to-substrate cohesion limit, so the films are flaked and partially broken.

To conclude, the α–Hf films containing up to 1 % of oxygen in solid solution have been prepared using magnetron sputtering of a hafnium target onto the substrates of silicon, glass ceramic, and mica. The films show an axial type texture with [001] axis normal to the film surface and the texture scattering angle equal or less 15 degrees. Using the X-ray strain measurements in the α–Hf films, the residual compressive stresses have been revealed which are an algebraic sum of the thermal stresses caused by the film-substrate system heating and the structural stresses due to both bombardment of the condensate by high-energy particles during the growth and formation of the secondary structure defects, i.e. the dislocation loops.

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Структура та напружений стан іонно-плазмових конденсатів гафнію

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Методом магнетронного розпилювання мішені з гафнію марки ГФЕ-1 іонами аргону одержано плівки товщиною 0,05–0,5 мкм на різних підкладках. Чистота одержаних плівок контролювалася рентгенівською флуоресцентною спектроскопією. Структура плівок досліджувалася рентгенівською дифрактометрією. Методом рентгенівської тензометрії у плівках α–Hf виявлено стискуючу залишкову напругу і визначено значення періодів кристалічної гратки.