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Study on resistivity and microstructure of magnetron sputtered *a*-C:Si films

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Electric resistivity and microstructure of silicon-doped (5 to 38 at. % Si) amorphous carbon (*a*-C) films deposited by dc magnetron sputtering in argon plasma of composed (graphite + single crystalline silicon) target has been studied as a function of silicon content in films. The film resistivity parallel and perpendicular to substrate surface was measured. The film structure was studied by electron diffraction and Raman spectroscopy. Doping with silicon did not influence the resistivity $\rho_{\perp}$ over the whole range of silicon concentrations studied, but resulted in marked increase in resistivity $\rho_{\parallel}$. Incorporation of silicon atoms into graphite-like cluster structure of carbon films results in distortion and disordering thereof in planes parallel to the substrate surface, thus promoting an increase in $\rho_{\parallel}$.

Исследованы электросопротивление и микроструктура легированных кремнием (от 5 до 38 ат. % Si) аморфных углеродных (*a*-C) пленок, осажденных методом магнетронного распыления на постоянном токе, в зависимости от концентрации кремния в пленках. Пленки получали распылением составной (графит + монокристаллический кремний) мишени в аргоновой плазме. Сопротивление пленок измерялось параллельно и перпендикулярно поверхности подложки. Структуру пленок изучали методами электронографии и комбинационного рассеяния света. Легирование кремнием не повлияло на удельное сопротивление $\rho_{\perp}$ во всем интервале концентраций кремния, но привело к резкому увеличению $\rho_{\parallel}$. Внедрение атомов кремния в структуру графитоподобных кластеров углеродных пленок6 приводит к ее искажению и разупорядочению в плоскостях, параллельных поверхности подложки, и, как следствие, способствует увеличению $\rho_{\parallel}$.

Amorphous carbon (*a*-C) films have a great application potential due to combination of specific properties, namely, high hardness, chemical inertness, high electrical resistance, and wide mobility gap. Among these, the electrical properties are of importance in view of possible application of *a*-C films in microelectronics. To use the *a*-C films in practice, it is necessary to know on the dependence of specific property on the deposition conditions, structure formation and evolution mechanisms in comparison with other film properties. Doping of *a*-C films with various elements (both metals and non-metals) is one of the ways to affect the structure and thus the properties of those films. Various techniques have been used in doping of *a*-C films, such as chemical vapor deposition (when the gas that contains doping element is introduced into gas mixture) [1–3], ion implantation of deposited films [4, 5], mass-separated ion-beam deposition (where the doping is performed by alternating direct deposition of low-en-

ergy $^{12}C^{+}$ ions and doping element ions) [6]. Doped a-C films have been produced also by magnetron sputtering of composite target [7, 8], and by filtered cathodic vacuum arc process [9, 10].

The deposition of Si-doped a-C and a-C:H films is of importance from both scientific and practical viewpoints since the materials in the carbon-silicon system are of good promise for use, e.g., as mechanical coatings due to their high hardness and low friction coefficient [9–13]. It has been shown that doping of carbon films with Si results in decrease in residual compressive stresses [9, 10], and improved Young modulus [10]. Incorporation of Si in a-C film reduces also the optical band gap [8] and changes film hardness [10, 14]. However, the electrical properties of a-C:Si films have not been systematically studied. Meanwhile, as was demonstrated earlier, the a-C films reveal pronounced anisotropy of electrical resistance depending essentially on the deposition conditions [15, 16] and doping with electrically active boron additive [17].

In this work, we have used magnetron sputtering of composed target to prepare silicon-doped carbon films. The effect of silicon concentration on the film resistivity is studied. Structural aspects of this effect are discussed, too.

The carbon films were deposited using a planar dc magnetron unit with a water-cooled target composed from graphite and chips of single crystal Si. The silicon amount in the composed target was adjusted so that the silicon concentration in deposited films varied in wide range (in our case, from 5 to 38 at. %) as determined by the electron-probe microanalysis (EPMA) method with Camebax SX-50 instrument. The target-to-substrate distance was 45 mm. The sputtering gas was 99.97 % pure argon at 1 Pa constant pressure. As substrates, polished platelets of Si–Ti–Al–O ceramic (for resistance measurements) and Si (111) single crystal plates (for structure study) were used.

The films were deposited on substrates mounted on substrate holder that allowed pre-sputtering of the target onto a shield in order to remove any contamination from the target surface and stabilize the magnetron discharge parameters. The magnetron unit was operated in optimum regime at about 100 W, and substrates were at a floating potential of approximately −30 V during film deposition. This provided minimization of non-controllable heating of growing films by plasma radiation and bombardment with positive ions. The film resistance was measured in two directions: parallel ($R_{\parallel}$) and perpendicular ($R_{\perp}$) to the substrate surface. For this purpose, the specially configured 150 nm thick nickel film contacts were magnetron sputtered onto substrates before carbon film deposition, and onto the surface of as-deposited carbon films [16, 17]. Such configuration of nickel electrodes made it possible to measure the resistance $R_{\perp}$ and $R_{\parallel}$ of carbon films. Carbon films resistivities $\rho_{\perp}$ and $\rho_{\parallel}$ were calculated in $\Omega\cdot$cm values from measured $R_{\perp}$ and $R_{\parallel}$ values taking into account the geometry and thickness of carbon film between metal contacts. The film thickness as measured using an optical interferometer was 400 to 600 nm. The film structure was examined by high-energy electron diffraction in reflection mode (RHEED) and Raman spectroscopy. In this study, the Raman scattering was induced by the λ = 488 nm line of an argon laser. Spectral measurements were taken at room temperature in the "back-scattering" configuration. The scattering signal was recorded using a cooled photomultiplier tube operating in the photon counting regime. The spectra were fitted with two Gaussian shape lines (G-band centered around 1580 cm^{-1} and D-band centered around 1355 cm^{-1}), taking into account linear background term.

Figure 1 shows the dependences of lg $\rho_{\perp}$ and lg $\rho_{\parallel}$ on concentration of Si in a-C films. As seen, $\rho_{\perp}$ is almost independent of Si content over the whole range of concentrations studied whereas $\rho_{\parallel}$ increases drastically. Structural study of Si-doped a-C films by RHEED have shown that these are amorphous within the entire range of Si concentrations examined, and the respective electron diffraction patterns look as several halos typical of amorphous structure. At the same time, Raman spectroscopy has shown that incorporation of Si atoms results in structural changes of a-C films. In Fig. 2, the typical Raman spectra are shown for low-doped (6 at. % Si) and high-doped (27 at. % Si) a-C films. The respective spectral parameters are listed in Table. The broad bands in the 1200–1700 cm^{-1} range were fitted with two Gaussian peaks known as the graphite (G) and disorder (D) peaks, respectively. Both spectra exhibite two-peak structure, and the G peak position shifts towards lower frequencies as silicon concentration in film increases, whereas the intensity ratio of D and G peaks, I_D/I_G, de-

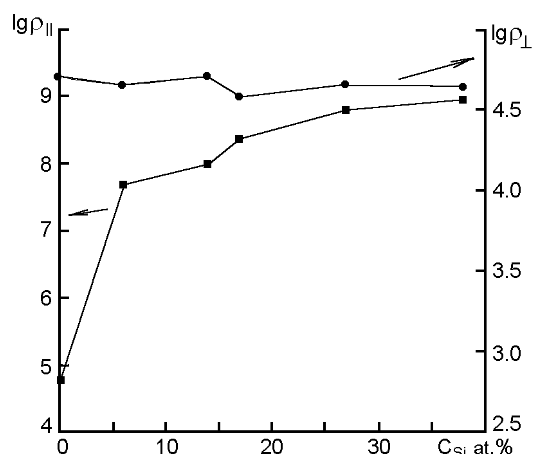

Fig. 1. Logarithm of resistivity $\rho_{\parallel}$ and $\rho_{\perp}$ as a function of silicon concentration in *a*-C films.

creases, and the *G* peak half-width increases.

The above observations can be explained within the frame of the structural model for disordered and amorphous carbon [18]. It has been shown by many studies [16, 19, 20] that the sputter-deposited *a*-C films have cluster structure with predominantly sp^2 bonds between carbon atoms. The fact that RHEED patterns in our study did not change with increasing Si concentration means that short-range atomic order in films remains unchanged and the cluster size is so small that structural changes within the clusters are below the method sensitivity limit. So, we followed the structural changes in films using Raman spectroscopy.

According to modern concepts, the Raman spectrum is considered to depend on clustering extent of the sp^2 phase, bond disordering, presence of sp^2 rings or chains, and the sp^2/sp^3 ratio. In the transformation of carbon structure from nanocrystalline graphite to amorphous carbon, the main features in the Raman spectrum evolution are the following: i) the *G* peak moves from ~1600 cm^{-1} to ~1510 cm^{-1}, and ii) the integral intensity ratio I_D/I_G decreases [18]. As is seen from our results (Fig. 2, Table 1), the spectrum with the lowest studied silicon content is pronouncedly two-peak one. The frequency position of *G* peak at 1582 cm^{-1} and integral intensity ratio I_D/I_G value of 1.12 indicate that, according to the model [18], the carbon film structure corresponds to the "nanocrystalline graphite/amorphous graphite" region. The Raman spectrum shape for the film with 27 at. % Si evidences presence of strongly disordered sp^2 clusters or their fragments within the film

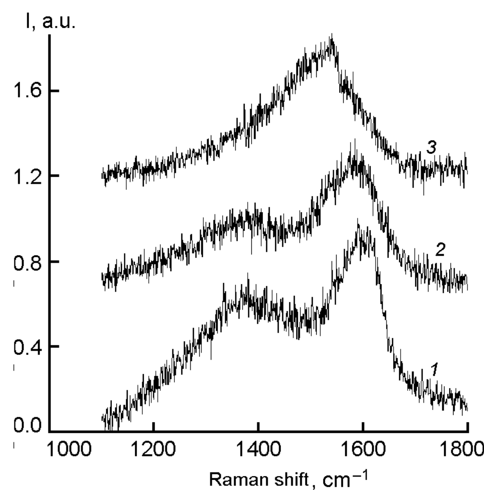

Fig. 2. Typical Raman spectra for low-doped and high-doped *a*-C films. Si concentration at. % *1* – 0; *2* – 6; *3* – 27.

Table. Raman spectra parameters for silicon-doped *a*-C films

Si, at. %	*G* peak position, cm^{-1}	I_D/I_G	*G* peak width, cm^{-1}
0	1596	2.17	86
6	1582	1.12	103
27	1532	0.67	125

structure. The position of *G* peak (1532 cm^{-1}) and integral intensity ratio I_D/I_G value (0.67) indicate that the film structure is almost entirely amorphous. This evidence is also confirmed by RHEED results: the respective ED patterns look as several halos. The structural information obtained from Raman spectra can explain the observations in Fig. 1. As was shown in [9, 10], silicon atoms incorporated in the carbon film substitute carbon atoms in aromatic rings. Since the silicon atomic radius is larger than that of carbon (0.133 nm and 0.077 nm, respectively) and the strength of Si–C bonds (3.21 eV) is lower than that of even sp^3 C–C bonds (3.70 eV) [21], thus, the incorporation of silicon atoms causes a structure distortion of sp^2 bonded carbon cluster. For the same reason, the Raman frequency shifts down with increasing concentration of Si in the film. When the Si concentration in the film is low, Si atoms can be expected to be distributed over the film volume homogeneously and isolated from each other. Accordingly, the film structure distortion due to presence of Si atoms will relax easily, and structural changes will be small. As the silicon concentration increases, more carbon atoms are sub-

stituted by silicon ones within sp^2-bonded carbon clusters, and a stronger distortion is produced in the film structure. As a result, the stretching mode vibration energy of the ring becomes reduced. This results in decreased intensity of D peak (i. e., decrease in I_D/I_G), shift of G peak towards lower frequencies, and increased width of that peak (Table). An increase in G peak width indicates also increase in bond angle and bond strength disorder at higher silicon content.

The above-mentioned evolution of carbon film structure under introduction of silicon atoms is consistent with observed resistance changes of those films. An increasing structure disorder in the a-C film with increasing silicon concentration results in increase in electrical resistance of those films. As can be suggested from Fig. 1, the structural changes occur mainly in the graphite-like planes within sp^2-bonded clusters, which are arranged parallel to the substrate surface [16]. There are virtually no structural changes in the direction perpendicular to graphite-like planes. The above changes in a-C film resistance are in agreement with structural changes in those films.

Thus, the effect of doping with silicon (5 to 38 at. % Si) on the electrical resistance and microstructure of amorphous carbon (a-C) films deposited by dc magnetron sputtering has been studied. Incorporation of Si atoms results in increasing distortion of sp^2-bonded clusters within the a-C films in the plane parallel to the substrate surface. This, in turn, causes increased film resistance in that direction. At low Si concentration, silicon atoms incorporated in film are fairly isolated from each other, and the film structure distortion is weak. As the silicon concentration increases, a stronger distortion is produced in the film structure. As a result, the $R_{\parallel}$ resistance of a-C film increases.

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Дослідження електроопору та мікроструктури *a*-C:Si плівок, одержаних магнетронним розпиленням

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Досліджено електроопір та мікроструктуру легованих кремнієм (від 5 до 38 ат. % Si) аморфних вуглецевих (*a*-C) плівок, нанесених методом магнетронного розпилення на постійному струмі, в залежності від концентрації кремнію у плівках. Плівки одержували розпиленням складної (графіт + монокристалічний кремній) мішені в аргоновій плазмі. Електроопір плівок вимірювався паралельно та перпендикулярно поверхні підкладки. Структуру плівок вивчали методами електронографії та комбінаційного розсіювання світла. Легування кремнієм не вплинуло на електроопір $\rho_\perp$ у всьому інтервалі концентрацій кремнію, але призвело до різкого підвищення $\rho_\|$. Проникнення атомів кремнію у структуру графітоподібних кластерів вуглецевих плівок призводить до її спотворення і розупорядкування у площинах, паралельних поверхні підкладки, та, як наслідок, сприяє підвищенню $\rho_\|$.