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Metal-carbon nanocomposite films for temperature sensing with enhanced functionality

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Metal-carbon nanocomposites are characterized by a number of unique properties, perspective for the various-type applications. Presented experimental data of the conductivity of amorphous tungsten- and niobium-containing carbon-silicon nanocomposite films show the possibility to design the advanced wide-range temperature sensors, which are expected to possess the chemical stability, biocompatibility, mechanical, and other properties typical for this class of materials. The investigated films were deposited onto polycrystalline substrates using combination of PECVD of siloxanes vapors and DC magnetron sputtering of metal target. The conductivity σ of the films, measured using standard 4-probe technique in the temperature range 80-400K, is characterized by the gradual decrease with temperature. The experimental $\sigma(T)$ dependences are well fitted by the universal exponential expression, $\sigma(T)= \sigma_0+aT^n$, where σ_0, a, and n are the fitting parameters dependent on the value of metal concentration. The conductivity mechanisms in the investigated amorphous metal-containing carbon-silicon nanocomposite films are discussed in the framework of the model of inelastic tunneling in amorphous insulators in the presence of the structural transformation in carbon-silicon matrix.

Key words: DLC, metal, nanocomposite, temperature sensor, inelastic tunneling

1. INTRODUCTION

Diamond-like carbon (DLC) films are widely used as protective coatings due to their attractive properties such as high hardness and wear resistance, low friction coefficient, chemical inertness and high electrical resistivity [1]. But the widespread use of DLC films is limited by high values of internal stress, poor adhesion to some of the substrates, etc. Some of the DLC films properties may be essentially improved by doping of the films by different elements [2]. Besides this is an effective way to enhance their functionality for further industrial applications.

The tribological properties of silicon- or, silicon and oxygen-incorporated DLC films were studied in [3-5]. It was shown that the films were characterized by the excellent surface smoothness compared to that at pure DLC films. The friction coefficient was less than 0.1.

Metal-containing DLC (Me-DLC) films are also interesting due to their surface morphology [6], mechanical properties [7] and electrical conductivity [8]. These properties are dependent on the metal concentration value.

The presented paper is devoted to the study of metal concentration influence on the electron transport mechanisms in the thin films of amorphous carbon-silicon nanocomposites containing tungsten and niobium. The possibilities of the application of the films as temperature sensors are discussed.

2. EXPERIMENTAL

2.1 Deposition

The 1 μm thick W- and Nb-containing amorphous carbon-silicon nanocomposite films were deposited onto polycrystalline substrates using the combination of PECVD of siloxane vapors and DC magnetron sputtering of metal target. The RF (1.76MHz) bias was applied to the substrate holder during deposition [9].

After deposition the samples were prepared for the resistivity measurements by RF (13.56MHz) Ar plasma etching using mechanical mask of the standard 4-probe geometry.

2.2 Raman spectroscopy

The room temperature (RT) structural measurements of the investigated films were performed by Raman spectroscopy in the range 800 – 1800 cm^{-1} using 632.8 nm He-Ne laser. The laser power was chosen around 20 mW in order not to influence the microstructure of the films [10].

2.3 R(T) dependences

The wide-temperature (80 – 400 K) electrical resistivity measurements of the amorphous metal-containing carbon-silicon nanocomposite films were carried out in a gas-flow cryostat using routine four-terminal low frequency AC lock-in technique. The mechanical contacts to the samples were used.

Metal concentration measurements were performed by Electron Probe Micro Analyzer (EPMA).

3. RESULTS

In Fig.1 the Raman spectra of the niobium-containing metal-carbon nanocomposite films are presented.

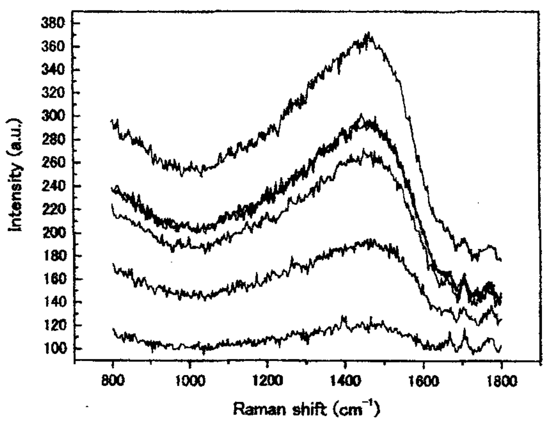

Fig.1 Raman spectra of Nb-containing amorphous metal-carbon nanocomposite films. The curves are shifted apart from each other for clarity. The Nb concentration in the films is shown near each curve.

They look as typical ones of a-C:H films being characterized by the broad peak positioned at 1400 – 1500 cm^{-1}. Each peak can be deconvoluted at two Gaussian peaks, one centered around 1350 cm^{-1}, another one at 1550 cm^{-1} (known as D and G peaks respectively) [1]. The Raman spectra of W-containing films look similar to those of Nb-containing ones and are not shown.

In Fig. 2 the wide-range dependences of the normalized resistivity $\rho(T)/\rho(300K)$ on temperature of Nb- and W-containing amorphous carbon-silicon nanocomposite films are shown. All dependences are characterized by the monotonic increase of the resisitivity with temperature decrease.

4. DISCUSSION

4.1 Structural analysis

Following EPMA data the conductivity of the metal-containing carbon-silicon nanocomposite films increases monotonically with metal concentration both for W and Nb-containing samples. In Fig.3 the dependence of RT conductivity of the Nb-containing films on metal concentration is shown. As it can be seen the conductivity is characterized by the power dependence over the entire Nb concentration range studied. This type of the conductivity *vs*. temperature dependence is typical for the metal-insulator composites.

In Fig. 4 the peak intensity ratio I(D)/I(G) of D and G peaks calculated from Raman spectra is shown for the films containing both W and Nb. As it can be seen the curves demonstrate the similar behavior with RT conductivity variation for both metals. When RT conductivity is less than 10^4 S/m, the I(D)/I(G) ratio is close to the constant value in the range 0.8 – 1.0. When RT conductivity exceeds 10^4 S/m, which corresponds to the metal concentration value close to 25 at. % the sharp growth of I(D)/I(G) is observed. This can mean that the microstructure of the carbon phase of host matrix is influenced by metal concentration.

As it was shown in [1], the value of I(D)/I(G) peak intensity ratio is determined by the average sp^2 cluster size. The observed increase of I(D)/I(G) up to 1.9 corresponds to the growth of the average sp^2 cluster size approximately from 1.2 to 1.7 nm. It is necessary to note, that the discussed I(D)/I(G) ratio is lower for the Nb-containing films. It can mean, that sp^2 clusters in the films, containing Nb are smaller, than that in W-containing films

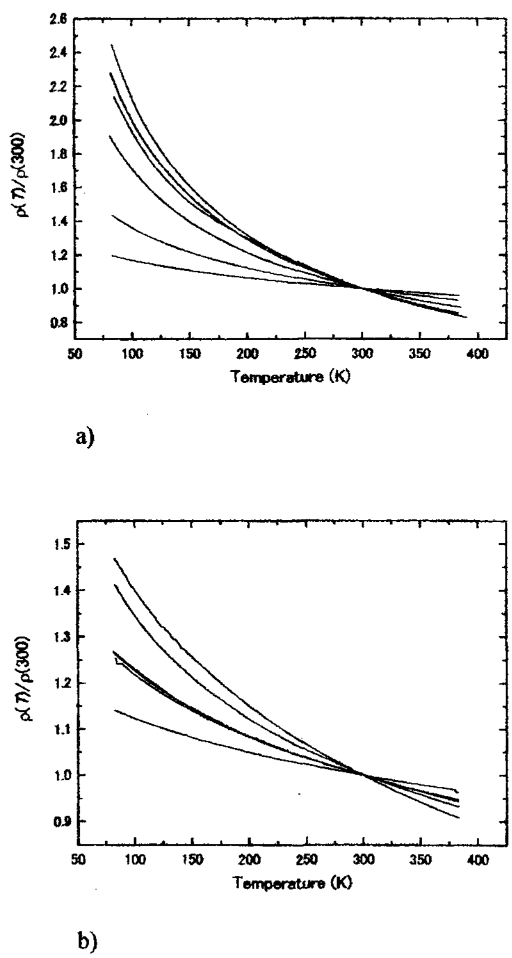

Fig.2 Temperature dependence of the normalized resistivity of:
a) - Nb-containing films,
b) - W-containing films.
The total resistivity variation $(\rho(80K)-\rho(400K))/\rho(300K)$ increases with metal concentration decrease.

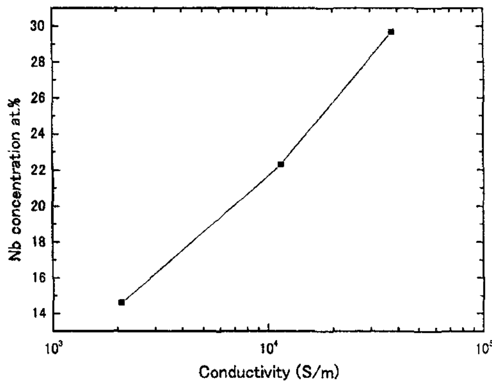

Fig.3 The dependence of RT conductivity of Nb containing film on metal concentration.

4.2 Electron transport

The structure of metal-containing carbon-silicon nanocomposites can be considered as consisting of the metal nanoclusters dispersed in the insulating carbon-silicon host matrix and being separated by the potential barriers. The electron transport in such system occurs via electron tunneling between metal nanoclusters. At the insulating side of the metal-insulator transition the temperature dependence of the conductivity follows the exponential expression [11] $\sigma = \sigma_0 \exp\left(-T_0/T\right)^{1/2}$, where T_0 – is temperature parameter.

However, due to the amorphous structure of the host matrix, the localized states exist in the intercluster potential barriers.

The conductivity of the granulated metal-insulator material determined by the tunneling of electrons through potential barriers between metal grains is dependent on the number of localized states n in the intercluster potential barriers and on the distances between metal clusters as well. It is described by the model of the resonant inelastic tunneling of the electrons [16].

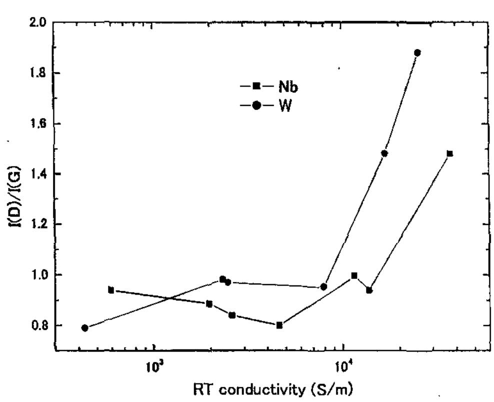

Fig.4 I(D)/I(G) peak ratio as a function of RT conductivity in metal-containing carbon-silicon nanocomposte films.

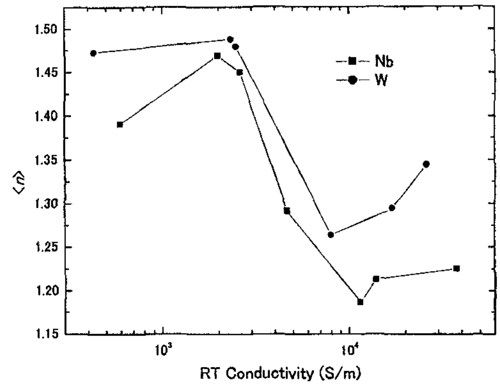

Fig.5 Average number $\langle n\rangle$ of localized states in the intercluster conducting channels of Nb- and W-containing amorphous carbon-silicon nanocomposite films.

In the framework of this model the conductivity follows the power-law expression

$$\sigma \sim aT^{p} \qquad (1),$$

where constants a, and p are dependent on the average number of the localized states $\langle n\rangle$ in the intercluster potential barriers. For p this dependence is given by the following expression [16]:

$$\langle n\rangle = \frac{1}{2}\left(p-1+\left(p^2+2p+9\right)^{\frac{1}{2}}\right) \qquad (2)$$

The experimental conductivity *vs.* temperature dependences of the investigated amorphous carbon-silicon nanocomposite films containing both tungsten and niobium are well fitted by the expression (1) over the entire range of temperature and metal concentration.

The calculated average number of the localized states in the intercluster conducting channels $\langle n\rangle$ is shown in Fig.5 as a function of RT conductivity of the films. Both Nb- and W-containing amorphous carbon-silicon nanocomposite films demonstrate the similar dependence of $\langle n\rangle$ on RT conductivity. However in the films containing Nb $\langle n\rangle$ is lower over the entire concentration range than that in W-containing films.

In the case of small metal concentration (RT conductivity less than $2\cdot10^3$ S/m) the slight increase of $\langle n\rangle$ is observed. At further metal concentration growth the decrease of $\langle n\rangle$ takes place. And finally at high values of metal concentration (RT conductivity exceeds $8\cdot10^3$ S/m) the increase of $\langle n\rangle$ is observed again.

It is evident from the simple geometric considerations that the average number of the localized states in the intercluster conducting channels should decrease with metal phase concentration increase in the case if the local density of the defects remains constant. The observed deviation of this behavior at high values of metal concentration can be explained by the generation of the new defect states.

The increase of the number of localized states between metal clusters can be associated with sp^2 phase growth, which takes place at high metal concentration. This follows from observed growth of I(D)/I(G) peak intensity ratio at high metal concentration (Fig. 4) as it was discussed above. Possibly the defect states are generated at the grain boundaries of graphitic clusters. This is consistent with the fact, that in Nb-containing films, where $\langle n \rangle$ is lower than in the films with W, the average sp^2 cluster size is smaller than that in W-containing films, as it was discussed earlier considering I(D)/I(G) peak intensity ratio.

The observed decrease of $\langle n \rangle$ at low metal concentration can be caused likely due to the fact that simple inelastic tunneling model can not be applied for the adequate description of the electron transport in the investigated films at low metal concentration. One of the possible reasons can be associated with the increasing role of the nanocluster charging energy.

4.3 Applications

As it can be seen from Fig.2 the experimental resisitivity *vs*. temperature dependences have the "soft" character. This makes the investigated metal-containing carbon-silicon nanocomposite films good candidates for the usage as wide-range temperature sensors. They will possess the mechanical and other properties close to the diamond-like carbon films. This will allow to use them under extreme environmental conditions.

The functionality of the temperature sensors can be enhanced by the possibility to fabricate the multilayered structures on the basis of metal-containing amorphous carbon-silicon nanocomposite films in order to combine the desired properties and to get principally new ones
The layers can be formed by the modulation of metal concentration and/or other deposition parameters
The multilayered structure of the sensors can essentially extend the range of their applications.

5. CONCLUSION

The electron transport properties of Nb- and W-containing carbon-silicon nanocomposite films were evaluated in the temperature range 80 - 400 K. The electron transport mechanism is discussed in terms of the intercluster inelastic tunneling model of the electrons in the presence of resonant localized states dispersed in the potential barriers between metal nanoclusters. The concentration dependence of the average number of the localized states in the conducting channels calculated in the framework of the inelastic tunneling model is discussed. The observed increase of the intercluster localized states concnetration at high metal concentration is associated with the sp^2 phase growth, which is confirmed by Raman spectra. It was also shown, that the films due to their smooth and "soft" character of the resistivity *vs*. temperature dependences are good candidates for the applications as temperature sensors. It is expected that the sensors will possess the high functionality typical for diamond-like carbon films.

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