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Cluster superconductivity in diamond-like carbon–silicon nanocomposites containing tungsten

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Abstract. It is shown that the nonhomogeneous structure of the superconducting phase in the diamond-like carbon–silicon nanocomposites containing tungsten with concentration close to the metal–insulator transition is responsible for the perculiarities in the character of the superconducting resistive response. The observed nontrivial quasireentrant resistive transitions can be explained in terms of the phase coherence destruction between the superconducting grains and by the renewal of superconducting phase generation at lower temperatures defined by the presence of the two scales of inhomogeneity in the investigated films. The resistance–current characteristics in the vicinity to the superconducting transition and magnetic measurements do not contradict the qualitative model proposed.

1. Introduction

The superconductivity in highly disordered and nonhomogeneneous materials belongs at present to the intensively studied phenomena. It is generally believed that the inhomogeneities are responsible for the modifications of the superconducting transition character, when the effective superconducting coherence length becomes comparable and less than the lengths characterizing inhomogeneities of the system. In this case strong space fluctuations of the order parameter would be expected in the system and the superconducting phase becomes essentially nonhomogeneous. It is in common practice to model the superconducting properties of such materials through the superconducting grains (s-grains). If the total volume of the superconducting phase is less than the value of the percolation threshold the resistivity does not fall to zero. In some cases it is possible to observe two superconducting transitions with different values of the critical temperature.

At low temperatures the depression of the phase coherence between separate s-grains may lead to a sharp resistance increase in the temperature range below the main superconducting transition. Such a resistance increase is called a quasireentrant transition and was presumably observed for the first time in [1].

The objects traditionally used for the investigations of inhomogeneity influence on superconducting properties are metal–dielectric films [2–4]. Metal exists in such films in the form of grains dispersed in an insulating matrix. The typical size, properties and the structure of metal grains and insulating matrix depend on the types of metal and dielectric and deposition conditions as well.

Diamond-like amorphous carbon may be of special interest as an amorphous insulating matrix for different metals. It contains mainly sp^3 (but also sp^2 and sp) carbon sites [5] and is characterized by very high fluctuations in a static potential due to the cluster structure, for which a model was proposed by Robertson [6]. Such fluctuations of the potential relief between metal grains may essentially modify the transport properties and superconducting response character.

The amorphous dielectric matrix of the investigated diamond-like carbon–silicon nanocomposite films contain carbon and silicon. The concentrations of sp^3 and sp^2 bonds of carbon atoms depend on deposition conditions and their ratio usually lies between 1 and 2. The presence of silicon imparts high stability to the diamond-like carbon matrix. Properties of the films were fully described in [7–9] Dorfman [7] proposed a model of the film structure, where carbon and silicon form two interpenetrating amorphous networks, whose dangling bonds are stabilized by hydrogen and oxygen respectively. The tungsten atoms are introduced into the carbon–silicon matrix as separate atoms at low tungsten concentrations. By an increase of the tungsten concentration up to the value of the percolation threshold and higher they form the third network—infinite conducting cluster.

At low tungsten concentrations the films are insulators with resistivity higher than 10^{14} Ω cm. The increase of tungsten concentration up to values of about 40 at.% and higher leads to the decrease of the resistivity down to 10^{-4} Ω cm. By this is meant that the metal–insulator (MI) transition, which occurs at a value of tungsten concentration around 16–18 at.%, is initiated by an increase of the tungsten content and can be related to the Mott type. However the increase of the tungsten concentration is connected with an increase of the tungsten atom flux near the surface of the films and with an increase of their average energy as well. This can lead to modifications of the film structure and to variation of the degree of disorder in metal clusters and in the dielectric matrix. Taking into account this fact one has to describe the MI transition in the investigated films in terms of combined Mott and Anderson metal–insulator transitions.

2. Experiment

The films with thickness about 1 μm were grown on rf-biased polycrystalline dielectric substrates (thickness around 250 μm) using plasma decomposition of polyphenylmethylsiloxane ($(CH_3)_3SiO(CH_3C_6H_5SiO)_3Si(CH_3)_3$) vapours in a DC diode reactor. Tungsten whose concentration could reach 50–60 at.% was introduced into the films during their growth using magnetron sputtering. Details of the growth process can be found in [7–9].

Contacts to the films for the electroconductivity measurements were prepared using silver paint. In order to enhance their adhesion and stability to the thermocycling in the wide temperature range the films with prepared contacts were annealed at temperature 200–250 °C for 10–15 minutes in a flow of nitrogen. Such heat treatment following [7, 8] does not lead to any changes in structural and electrophysical properties of the investigated films.

The electroconductivity measurements were performed by an application of the usual four-terminal technique both in DC and AC lock-in regimes.

The dynamic magnetic susceptibility was measured at frequency 333 Hz. No dependence of the output signal on the frequency up to 10 kHz was found. The magnitude of alternating applied magnetic field was about 10^{-2} Oe. The possibility of applying an additional constant magnetic field with magnitude up to 2 Oe during measurements allowed us to investigate the influence of weak magnetic fields on the magnetic superconducting response character.

3. Results

It was found that investigated diamond-like carbon–silicon nanocomposite films containing tungsten with an average concentration $N_w > 16$ at.% demonstrated the superconducting resistive transition with critical temperatures $T_c < 5$ K depending on tungsten concentration. The character of the superconducting transition changed from practically symmetrical to the nonsymmetrical two-step one while tungsten concentration was decreased from value of about 40–50 down to 16 at.%. A typical example of the observed two-step superconducting transition for the case of tungsten concentration of about 17 at.% is shown in figure 1. The presented superconducting transition is characterized by two critical temperatures measured at the middle of the resistance variation—3.65 and 2.4 K respectively.

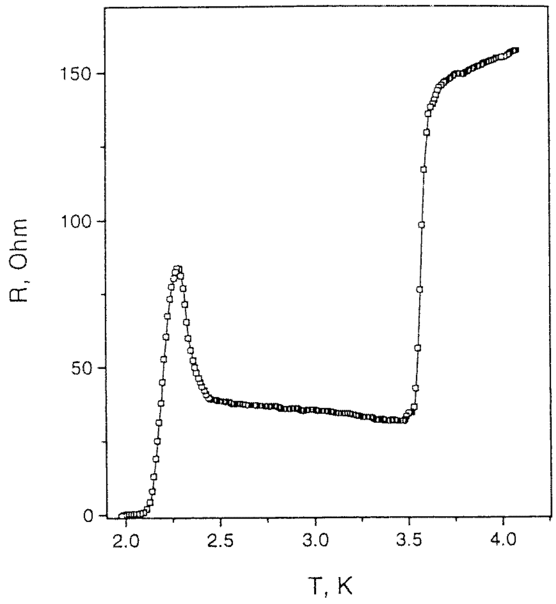
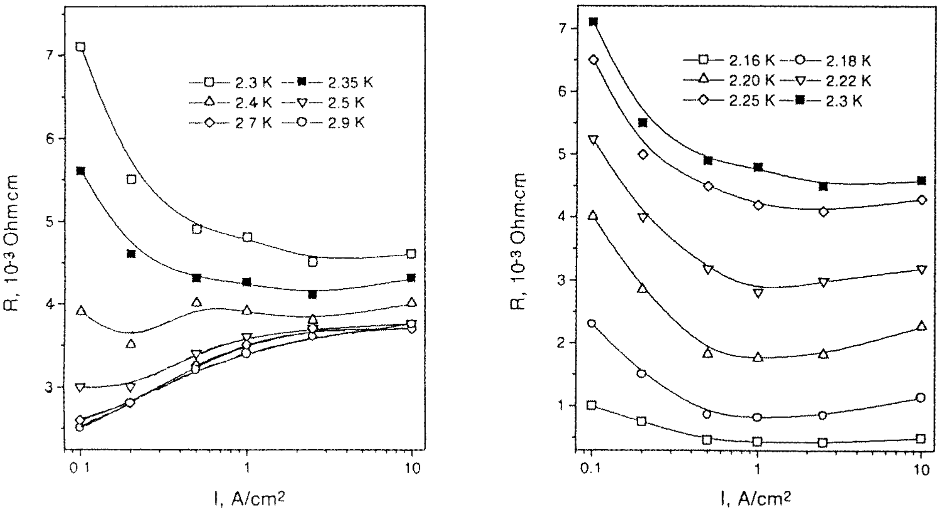


Figure 1. Two-step resistive superconducting transition in the diamond-like carbon films containing tungsten with concentration 17 at.%.

To the peculiarities of the discussed transition can be related the existence of the sharp resistance increase (about twofold) in the vicinity of the second transition. The resistance in the range of the observed maximum strongly depends on the transport current across the sample.

In figures 2(a) and 2(b) are displayed the resistance–current characteristics (where $R = U/I$) for the temperature range in the neighbourhood of the resistance maximum observed. In figure 2(a) $R(I)$ curves for the temperature range $2.3 < T < 2.9$ K (the region below the main superconducting transition and before the quasireentrant peak) are shown. $R(I)$ curves for the temperature range $2.16 < T < 2.3$ K are depicted in figure 2(b). It can be seen that the resistance of the investigated films depends on the transport current in the temperature range below the main superconducting transition and the character of the resistance–current dependences drastically changes passing through the temperature of the resistance maximum.



(a) (b)

Figure 2. Dependences of the resistance on transport current in the diamond-like carbon films containing tungsten ($N_W \approx 17$ at.%) at different temperatures in the temperature range below the main superconducting transition: (a) $T = 2.3$–2.9 K; (b) $T = 2.16$–2.3 K.

There can be distinguished two parts of different $R(I)$ behaviour. The first part ($I < 3$ A cm^{-2}) is characterized by a resistance increase for temperatures in the range 2.5–2.9 K which is replaced by a decrease of the resistance at $T < 2.4$ K. Such a form of $R(I)$ dependence is retained by further lowering of the temperature down to 2.16 K but the amplitude of R diminution is decreased. The intermediate behaviour of $R(I)$ is observed at 2.5–2.3 K where $R(I)$ has a marked minimum at the currents about (2–3) $\times$ 10^{-1} A cm^{-2}.

For the currents in the range (1–3)–(1–3) $\times$ 10^{-1} A cm^{-2} the resistance slightly increases with the current at temperatures 2.9–2.18 K and is constant in the temperature range $T < 2.18$ K.

In figure 3 are presented the dependences of the magnetic susceptibility on the temperature for different values of the external constant magnetic field in the temperature range below the main resistive superconducting transition.

At low magnitudes of the applied magnetic field the superconducting transition has a well expressed two-step form with critical temperatures essentially lower (2.6 and 1.5 K respectively) than critical temperatures of the resistive superconducting transition (figure 1). By an increase of the applied magnetic field the first transition is completely suppressed and there remains only the second superconducting transition with critical temperature around 1.5 K in the magnetic field $H > 2$ Oe. It should be pointed out that at the temperature corresponding to the temperature of the resistance maximum no perculiarities in $\chi(T)$ dependences were observed.

4. Discussions

It is generally agreed that the superconductivity in metal–insulator mixtures can be described as a homogeneous one when $\xi_{sc} > \xi_p$ where ξ_{sc} is an effective supercoducting coherence length of the medium and ξ_p is a correlation length, which diverges at the point of MI transition v_p as $|v - v_p|^{-\nu}$, where v and ν are volume fraction of metal and critical index

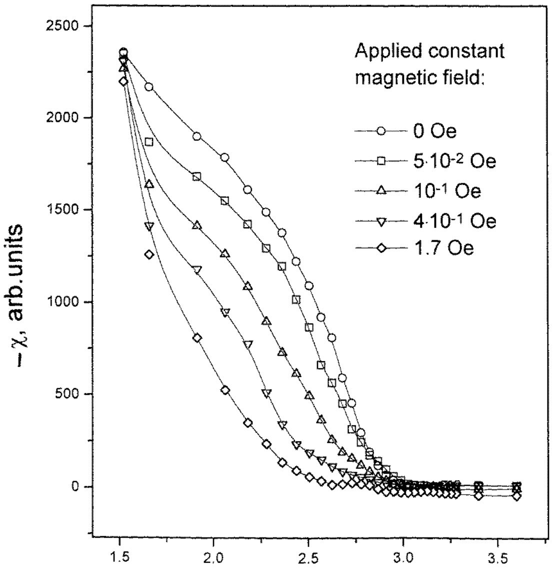


Figure 3. The evolution of the superconducting magnetic response in the diamond-like films containing tungsten ($N_W \approx 17$ at.%) by an increase of constant magnetic field.

respectively. In this case the particular structure of the conducting cluster is unimportant and the superconductivity can be described in terms of dirty superconductors [10].

Otherwise if $\xi_{sc} < \xi_p$ the superconductivity is essentially nonhomogeneous. In the case $d < \xi_{sc} < \xi_p$ (where d is a typical size of metal grains) the superconducting phase is characterized by strong space fluctuations of order parameter and can be modelled through s-grains with different critical temperatures. In this model the total volume of the superconducting phase increases as temperature is decreased. When s-phase volume reaches the value of s-percolation threshold v_s the infinite superconducting cluster is formed on the fractal of the infinite conducting cluster and the resistive superconducting transition is observed.

As the MI transition is reached the influence of localization effects, manifested as degradation of the critical temperature, the enhancement of s-transition broadening and nonsymmetry, increases. Localization brings about the shift of the MI transition point towards higher metal concentrations [11]. However the values of the tungsten concentration at the MI transition point in the investigated films are close to those of the classical percolation threshold [7]. This allows the infinite conducting and superconducting clusters to have the particular low-density structure, which can lead to the decrease of the percolation threshold—e.g. needle shaped or quasi-one-dimensional structure.

The enhancement of the s-phase volume with temperature decrease may be accompanied by the Josephson coupling (j-coupling) between separate s-grains when the Josephson energy E_j exceeds kT.

When the total volume of s-phase is not enough for the infinite s-cluster formation the resistivity is not equal to zero after the resistive transition. The magnitude of the resistance after s-transition depends in this case on the proximity of the system to MI transition point. If E_j is lower than the critical temperature, the second step of s-transition, determined by the temperature of the global phase coherence establishment, can be observed.

Some information about the structure of the s-phase can be obtained from the combined analysis of the resistance–current $R(I)$ and dynamic magnetic susceptibility $\chi(T, H)$ characteristics in the same temperature range.

There was observed no singularity in $\chi(T)$ dependences at temperatures around 3.65 K, which correspond to the main resistive superconducting transition. Two possible explanations of this fact can be given. The first one can be connected with the relatively small volume of s-phase determined by the special features of s-cluster structure, as mentioned above, whose topology in turn is determined by the structure of the infinite conducting cluster.

Another explanation is based on the assumption that the penetration depth of the magnetic field λ exceeds the typical size of s-grains $l(\lambda \gg l)$. Magnetic susceptibility is proportional in this case to a factor $(l/\lambda)^2 \ll l$ and allows us to estimate the upper value of the typical s-grain size. The magnetic susceptibility of the system composed from s-grains at the percolation threshold is given by the following expression [17]:

$$\chi = -v_p(l/\lambda)^2/10\pi. \tag{1}$$

For the sensitivity $\Delta\chi/\chi$, about 10^{-3}, of the equipment used, for the classical value of the percolation threshold 0.17 and the value of penetration depth λ not greater than 10^{-4} cm, the typical size of s-grains does not exceed 500 Å. This value satisfies the criterion $1 > d$ mentioned earlier. It is necessary to note that this estimation is not contradictory to the assumption about the quasi-one-dimensional structure of the s-cluster.

As is evident from figure 1 $R(T)$ dependence is characterized by a relatively small value of $\mathrm{d}R(T)/\mathrm{d}T$ in the temperature range 2.9–2.4 K. This suggests that s-phase volume is little affected in this temperature range. However $\chi(T)$ measurements (figure 3) demonstrate an enhancement of the s-phase volume in the temperature range 3.0–2.0 K, which is most likely determined by the j-bond generation because of weak magnetic field resulting in their destruction.

These data are not in conflict if the formation of j-bonds is accompanied by the enhancement of the number of superconducting loops where j-bonds play a role of weak links. S-loops are concentrated mainly in dead ends and do not lead to the effective shunting of the current-carrying backbone of s-clusters.

$R(I)$ dependences presented in figure 2(a) demonstrate the evolution of the resistivity against transport current across the films at different temperatures in the temperature range between the main superconducting transition and resistance maximum ($2.3 < T < 2.9$ K). The observed resistance increase in the range of small currents ($I < 1$ A cm^{-2}) and temperatures $T \geqslant 2.5$ K can be caused by the destruction of j-bonds by the transport current. The $R(I)$ dependence for j-contact with normal resistivity R_n between two equal superconductors for the currents higher than the critical current i_m is given in the form [12]

$$R = R_n(1 - (i_m/i)^2)^{1/2} \tag{2}$$

and tends to R_n when current is increased. The small value of the critical current in the system of s-clusters can be connected with the relatively small number of current-carrying channels at temperatures $T \geqslant 2.5$ K.

It is possible also to explain the observed resistance increase by a destruction of the superconductivity in the separate s-grains owing to the relatively high local density of the transport current in percolation structures exceeding the critical current of s-grains

The sharp resistance increase in the temperature range $T < 2.4$ K can be connected with the depression of the phase coherence between separate s-grains. Such a depression may be caused by the fluctuation of normal resistance R_n [13] which can be enhanced owing to the cluster sp^3–sp^2 structure of the dielectric carbon–silicon matrix [6] or by Coulomb charging effects between separate s-grains [14]. In both cases the current is determined by single-particle tunnelling. By an increase of the voltage between neighbouring s-grains and when $eV > 2\Delta$ or $eV > 2\Delta + E_c$ (where Δ and E_c are a superconducting gap and Coulomb charging energy respectively) the resistance rapidly decreases down to the value R_n of the intergrain tunnelling resistance. The observed decrease of the resistance shown in figures 2(a) and 2(b) for the temperatures $T < 2.4$ K can be determined by these processes.

The sharpness of the observed reentrant increase of the resistance confirms the assumption about the relatively small number of current-carrying s-channels whose destruction leads to the behaviour of such type. The value of $\mathrm{d}R(T)/\mathrm{d}T$ in the investigated films in the temperature range of the quasireentrant transition is rather high and reaches near the beginning of it the value $\sim 3\ R_0\ \mathrm{K}^{-1}$, where R_0 is the normal resistance of the film before the main superconducting transition. For comparison the same parameter for quasireentrant transitions in thin films of Pb, Al, In and Ga is not greater than $5 \times 10^{-1}\ R_0\ \mathrm{K}^{-1}$ [15] and for Sn films $2.0 \times 10^{-1}\ R_0\ \mathrm{K}^{-1}$ [16].

Indirect evidence of the quasi-one-dimensional structure of s-clusters can be also given by the absence of the manifestation of s-phase volume decrease (with sensitivity no less than 10^{-3}) due to the j-bond destruction in the $\chi(T)$ dependences (figure 3).

As can be seen in figure 1 the sharp drop of the resistance below the temperature $T = 2.3$ K is observed. It is reasonable to suppose that this decrease of $R(T)$ is connected with shunting of the broken j-bonds of the s-cluster by the new s-phase generated while temperature decreases. Such a point of view is confirmed by the increase of s-phase volume on $\chi(T, H)$ ($T_{c2} \approx 1.5$ K and shifted from $T_{c2} \approx 2.2$ K defined from $R(T)$ curves) dependences (figure 3) and by the decrease of the single-particle tunnelling contribution in $R(I)$ dependences at temperatures $T < 2.4$ K (figure 2(b)) when the character of $R(I)$ diminution is retained but its magnitude decreases with temperature.

It is possible to suppose two mechanisms of s-phase volume increase by temperature diminution. The first one is connected with the existence of the chemical compounds such as W_xC_y, W_xSi_y and W_xO_y, which are superconductors and have critical temperatures in the range 2–10 K depending on their composition and structure [18–20]. The first critical temperature T_{c1} is connected e.g. with the grains of amorphous tungsten, which can have the critical temperatures up to 5 K [21] whereas T_{c2} is defined by the presence of the above-mentioned compounds formed during growth of the film. The absence of perceptible amounts of any types of chemical compound was reported in [7] in the case of tungsten concentrations at least in the vicinity of the MI transition.

Nevertheless even small amounts of the superconducting chemical compounds may play an essential role in the modification of the s-cluster structure in the case when they are not dispersed randomly in the film but are formed e.g. at the metal grain–carbon–silicon matrix interface during film growth. The observed difference of the first and second resistive s-transition manifestations in $\chi(T)$ dependences may be indirect evidence that the increase of s-phase volume at the second s-transition is not a simple generation of a new s-phase as at the first critical temperature but the renewal of growth of s-grains which had already been formed at T_{c1}.

Another model of s-phase volume increase based on the existence of two scales of inhomogeneity can be described in terms of the layered structure, where two different lengths ξ_1 and ξ_2 characterize the proximity to the MI transition point of different layers of the material. If e.g. $\xi_2 > \xi_1$ the superconducting phase associated with ξ_2 will appear at $T_{c2} < T_{c1}$, where T_{c1} is a critical temperature corresponding to ξ_1. If T_{c2} is lower than the temperature of the resistance increase at 2.4 K a maximum in $R(T)$ dependences can be observed. The formation of the layered structure discovered in the granular metal–insulator composite films of Al–Te [22] in a wide range of Al concentrations confirm this model.

As shown in [23] the peculiarities in the upper critical magnetic field dependences can be explained in terms of the layered nonhomogeneous structure arising from the normal to the film surface modulation of the tungsten concentration. Such inhomogeneties can appear as a result of metal segregation during film growth or from the uncontrolled fluctuations of the deposition parameters.

It is not improbable that both mechanisms (the existence of different chemical superconducting compounds and the presence of layered structure) are involved in the formation of s-response of diamond-like carbon–silicon nanocomposites containing tungsten.

5. Conclusion

We studied the resistance and magnetic responses in diamond-like films containing tungsten in the range of tungsten concentrations close to the metal–insulator transition point. The observed sharp maximum in $R(T)$ dependences may be a result of two conflicting processes: a decrease of the s-phase volume due to the destruction of the phase coherence between separate s-grains and an increase of it on account of the second superconducting transition, of which the critical temperature is lower than that of the first one. The data on magnetic susceptibility and resistance–current characteristics do not contradict this qualitative model.

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