Microwave properties of granular amorphous carbon films with cobalt nanoparticles

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We have studied losses of microwave electromagnetic radiation in granular amorphous hydrogenated carbon films *a*-C:H(Co) containing cobalt nanoparticles at cobalt concentrations below the percolation threshold and in the percolation threshold region. The difference between the experimental values of the losses in granular structures sputtered on corundum-based substrates and those on aramide tissues is observed. It is found that this is determined by the difference in localization sizes of cluster electron states in *a*-C:H(Co) films. We have found that losses grow with increasing concentration of cobalt nanoparticles and with increasing frequency. The frequency dependence of losses is determined by the fast spin relaxation of nanoparticles. The anisotropy of losses in *a*-C:H(Co) covers on aramide tissues is observed. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1913797]

I. INTRODUCTION

Granular structures containing ferromagnetic nanoparticles of 3*d* metals in an isolating amorphous matrix show various interesting microwave properties. Among these is the effective absorption of electromagnetic waves at microwave frequencies, which allows us to consider granular structures as perspective materials for thin broad-band absorbing covers. High values of the microwave electromagnetic wave absorption is caused by the dielectric and magnetic losses in granular structures. The magnetic losses are due to the fast spin relaxation of nanoparticles determined by the spin-polarized relaxation mechanism.[1–3] Large dielectric losses in granular structures near the percolation threshold are determined by electron polarization on cluster electron states (CESs). These states are formed by *s* and *p* electrons of metal outer shells in nanoparticles and by electrons in localized states of defects and impurities in interparticle regions of the matrix.[1,4] Large localization sizes of CESs give high values of real and imaginary parts of the dielectric constant. In addition to this, the electromagnetic wave absorption in granular structures strongly depends on the sputtering technology and substrates.

Carbon granular structures with Co nanoparticles are good systems to investigate magnetic properties, magnetoresistance effects, conduction mechanisms, and microwave adsorption.[3,5–7] In the present work, we have analyzed experimentally the losses of electromagnetic waves in granular amorphous hydrogenated carbon structures *a*-C:H(Co) containing cobalt nanoparticles sputtered on corundum-based substrates and aramide tissues. Amorphous hydrogenated carbon *a*-C:H is the amorphous organic semiconductor the energy band structure of which is determined and can change with the content of hydrogen.[8] *a*-C:H is in the isolator state when the hydrogen content is high. We have studied *a*-C:H(Co) structures below the percolation threshold and in the percolation threshold region. Losses were measured on the open-circuit microstrip line and by the horn irradiation method. The results presented here confirm that the experiment dependencies can be accounted for in terms of the cluster electron state model and the spin-polarized relaxation mechanism. We have found that the two different substrates—a polycrystalline corundum-based substrates and an aramide tissue—induce different properties of the *a*-C:H(Co) coatings. This can be accounted for by the difference in localization sizes of CESs in the *a*-C:H(Co) coatings and results in different microwave loss properties. Losses grow with increasing concentration of cobalt nanoparticles and with increasing frequency. The frequency dependence of losses is determined by the frequency dependence of the spin relaxation of nanoparticles. We have observed the anisotropy of losses in *a*-C:H(Co) covers on aramide tissues. The nature of this effect is not comprehensively clear. It is supposed that the anisotropy of losses can be caused by the magnetic anisotropy of Co particles that originated from the hcp structure.

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II. PREPARATION OF GRANULAR FILMS

Experimental investigations were performed on the samples of amorphous hydrogenated carbon containing cobalt nanoparticles, designated as *a*-C:H(Co). The *a*-C:H(Co) films were grown on polycrystal corundum-based substrates and on aramide tissues by dc magnetron sputtering of composite graphite and cobalt targets in an argon-hydrogen plasma (80% Ar+20% H_2). The concentration of cobalt in the amorphous carbon deposit was controlled by changing the ratio of cobalt and graphite target areas. The films were deposited onto substrates heated to 200 °C. Prior to the deposition process, the chamber was evacuated to a base pressure of 1 μTorr. The samples were prepared in a working gas flowing at a pressure of 10 mTorr and an ion current density of 10^{-1} A/cm^2. The *a*-C:H(Co) film growth rate depended on the amount of cobalt introduced into the composition and varied in our experiments between 1.4 and 3.0 nm/min.

The film composition was determined by nuclear-physical methods of elemental analysis employing charged particle beams. The cobalt to carbon atomic ratio was determined by Rutherford backscattering using protons with a primary energy of E_p=1 MeV. In addition to the main controlled components, the films contained oxygen and nitrogen impurities. The impurity concentrations were determined by the method of nuclear reactions with deuterons at E_d =1 MeV: $^{16}O(d,p)^{17}O$; $^{14}N(d,p)^{15}N$; $^{12}C(d,p)^{13}C$. This technique is described in more detail in (Ref. 9). Based on these data, we determined the ratio of the number of cobalt atoms to the total number of atoms determined by methods of elemental analysis. For the samples studied, the content of cobalt atoms x varies from 20 at. % to 61 at. %, which corresponded to a cluster structure below the percolation threshold and in the percolation threshold region. The size of cobalt particles is determined from the small-angle x-ray scattering (SAXS) measurements.

The *a*-C:H(Co) films on corundum-based substrates have a thickness of 0.64–0.81 μm. The size of cobalt particles increases with x—from 2.2 nm at x =20 at. % to 3.5 nm at x=61 at. %.[4] The ensemble of cobalt ferromagnetic particles in the films was in the superparamagnetic state.

a-C:H(Co) sputtering on aramide tissues provides high flexible and durable electromagnetic absorption coverings. In order to measure the Co concentration in *a*-C:H(Co) films by nuclear-physical methods and to control the thickness of the sputtered *a*-C:H(Co) films on filaments, we made simultaneous depositions on Si substrates and on glass substrates, respectively. The microstructure of *a*-C:H(Co) films on an aramide filament was observed using the electronic microscope JSM-35 (Fig. 1). It is found that sizes of Co particles are in the range of 80–800 nm. Using depositions on glass substrates, we have found that the thickness of the sputtered *a*-C:H(Co) films varies from 0.85 to 2.1 μm.

III. ELECTROMAGNETIC MODE ABSORPTION ON A MICROSTRIP LINE

The electromagnetic mode absorption was measured on the open-circuit 50-Ω microstrip line shown in Fig. 2. The frequency range is 2–18 GHz. The microstrip width is 1 mm. At the given frequency range only the single electromagnetic mode can propagate along the microstrip. We measured the absorption of the electromagnetic mode in samples with the longitudinal size d=10 mm. Samples of *a*-C:H(Co) films on corundum-based substrates are put onto the microstrip so as *a*-C:H(Co) films are close to the microstrip line. In the case of *a*-C:H(Co) films sputtered on aramide tissues, in order to increase the precision of the experiment we put four layers onto the microstrip. To find losses of the electromagnetic mode propagated along the microstrip, we measure the incident and reflected waves. The losses in decibel units are defined as

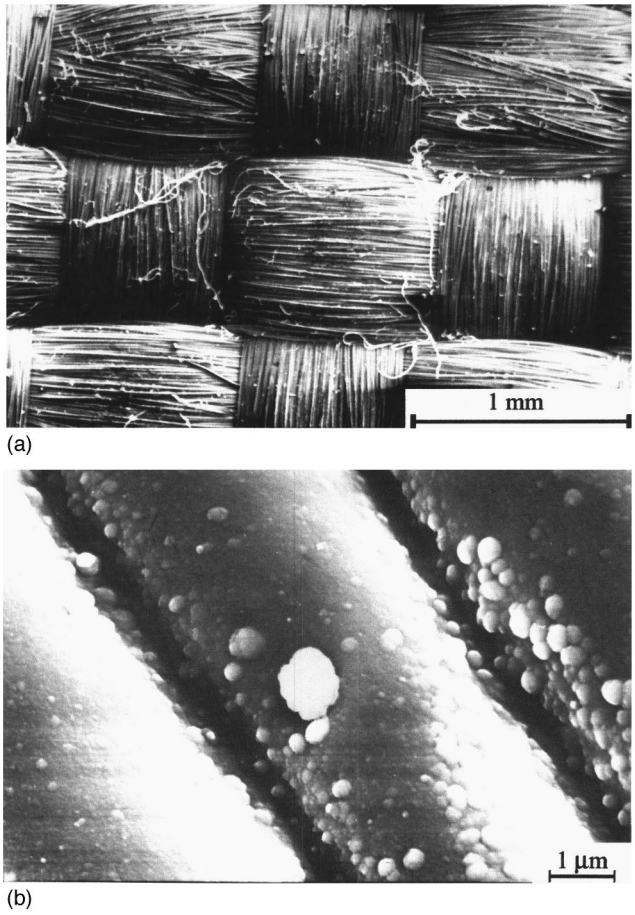

FIG. 1. *a*-C:H(Co) film with the thickness of 1.2 μm on filaments and with a Co concentration of 60 at. % deposited onto an aramide tissue. (a) tissue structure; (b) *a*-C:H(Co) cover on filaments.

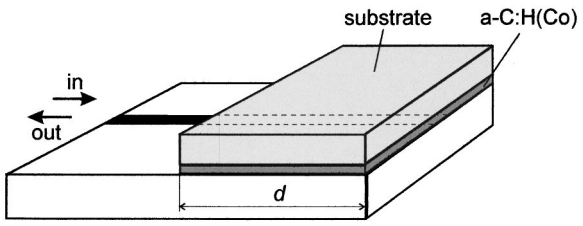

FIG. 2. Open-circuit microstrip line with *a*-C:H(Co) sample.

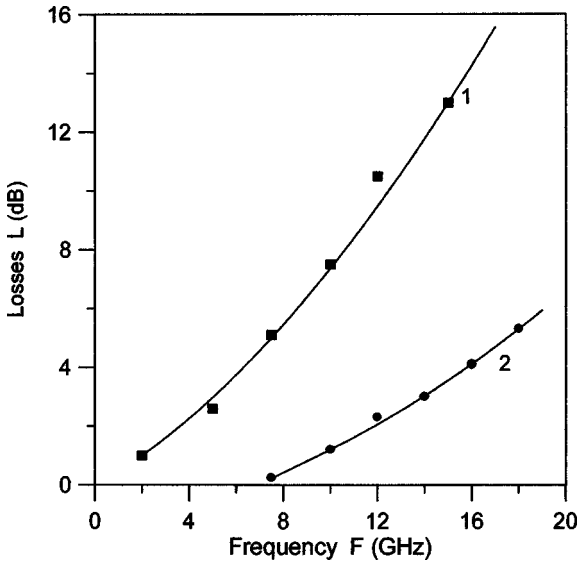

FIG. 3. Frequency dependence of the losses L of the electromagnetic mode propagated along the microstrip line with the a-C:H(Co) film:1—on polycrystal corundum based substrate (thickness of the film is 0.64 μm, 61-at. % Co); 2—on aramide tissue (four layers, thickness of the film on filaments is 1.2 μm, 60-at. % Co). Solid curves are theoretical approximations based on the spin-polarized relaxation model.

$$L = -10 \lg\left\{\frac{W_R}{W}\right\}, \tag{1}$$

where W and W_R are powers of incident and reflected waves, respectively.

It is found that a-C:H(Co) films sputtered on corundum-based substrates have higher losses L than do films with the same Co content sputtered on aramide tissues (Fig. 3). Since the anisotropy of the losses in a-C:H(Co) covers on aramide tissues is revealed, the samples are placed on the microstrip so that the maximum values of the losses are observed. The difference between the losses in a-C:H(Co) films sputtered on corundum-based substrates and the losses in films with the same thickness and Co content sputtered on aramide tissues can be accounted for by higher values of real and imaginary parts, ε', ε'', of the dielectric constant of films on corundum-based substrates and by different values of the spin-polarized decay constant. ε', ε'' are proportional to the localization size of CESs.[1,4] If there are direct contacts between particles or if electron tunneling transparency between particles is high, electrons can be localized on groups (clusters) of particles and form electron states—CESs. CESs are formed by wave functions of s and p electrons of Co outer shells in particles near the Fermi level and by electrons of matrix-localized states of defects and impurities in the interparticle regions. Groups of particles with CESs result in the formation of regions with high conductivity. The increase of the metal concentration leads to increasing electron tunneling transparency between particles, and the characteristic localization size of CESs grows. Below and at the percolation threshold the conductivity of a-C:H(Co) granular films grows with increasing characteristic localization size of CESs. In the percolation threshold region, the characteristic localization size of CESs becomes infinite. The electrons in CESs can be polarized by an electric field. Groups of particles with CESs have electric dipole momenta exceeding those of particle dipoles. The polarization of electric dipoles of particle groups with CESs determines the dielectric constant $\varepsilon = \varepsilon' + i\varepsilon''$ of the a-C:H(Co) structure. In the percolation threshold region, a sharp growth of the localization size of CESs leads to a sharp increase in ε.

In addition to this, at the percolation threshold granular films have high values of the magnetic permeability μ. These high values are determined by the fast spin-polarized relaxation of Co d-electron spins and by high values of the magnetization of Co particles.[1,2] For a-C:H(Co) granular films the spin-polarized relaxation is due to spin-flip electronic transitions between sublevels of thermally activated electronic clouds in Co particle neighborhoods in the matrix.[10] In the first approximation, at the studied frequency range the decay constant of spin-polarized excitations grows with increasing frequency F as $F(F-\gamma H_i)^{2/3}$, where $\gamma = 2.83$ MHz/Oe is the gyromagnetic ratio and H_i is the internal magnetic field acting on Co particles.[2] High values of ε', ε'', and μ' give high values of the microwave absorption L for films on corundum-based substrates in the percolation threshold region, where the Co concentration is in the range of 50–60 at. %, and the fast spin-polarized relaxation results in the growth of absorption losses L with increasing frequency F,

$$L = AF(F - \gamma H_i)^{2/3}, \tag{2}$$

where the coefficient A depends on the ε', ε'', μ', conductivity, temperature, density of localized states in the matrix a-C:H, and exchange interaction. In Fig. 3 for the a-C:H(Co) film on the corundum-based substrate we approximate the experimental values of the losses by the function (2) with the field $H_i = -2.88$ kOe.

As it was mentioned above, the losses of the electromagnetic mode in a-C:H(Co) films on aramide tissues are lower in comparison with the losses in films with the same Co content sputtered on corundum substrates. This can be explained by the difference in the CES forming. CESs in the a-C:H(Co) granular film on an aramide filament are hardly formed than CESs in the granular film on corundum-based substrates. The film on the corundum-based substrate shown in Fig. 3 is in the percolation threshold region, and the characteristic localization size of CESs for this film becomes infinite. The characteristic localization size of CESs for the film on the aramide tissue is limited by the filament thickness and by the wickerwork structure of the tissue. As a result of this, despite of the greater sizes of particles, smaller localization sizes of CESs in the a-C:H(Co) film on aramide filaments give low values of the dielectric constant and of the conductivity. This causes a decrease of the electromagnetic mode absorption L. We have found that the conductivity of a-C:H(Co) films on aramide tissues decreases by three orders in comparison with the conductivity of the same granular films sputtered on corundum substrates. In Fig. 3, for the a-C:H(Co) cover on the aramide tissue the experiment values of losses are approximated by the function (2) with the inner magnetic field $H_i = 2.54$ kOe. The inner magnetic field H_i acting on Co particles in covers on corundum substrates and aramide tissues have different signs. This can be ex-

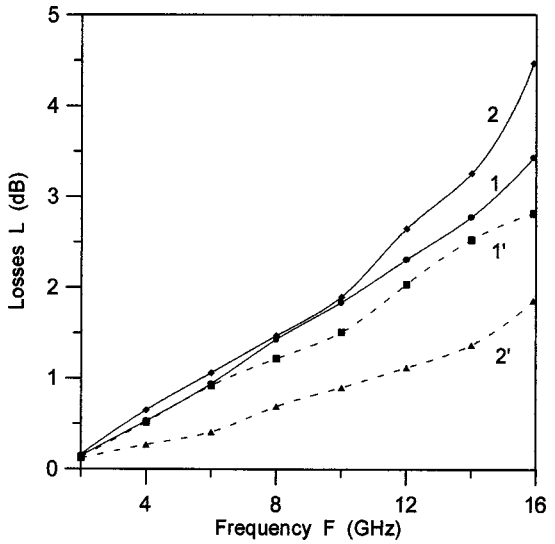

FIG. 4. Frequency dependence of the maximum (1,2) and minimum (1′,2′) values of losses L of the electromagnetic mode propagated along the microstrip line, which is loaded by four-layer a-C:H(Co) sputtered on the aramide tissue. The a-C:H(Co) film thickness on aramide filaments and the Co content are: 1—0.85 μm, 48-at. % Co; 2—0.93 μm, 60-at. % Co. 1′, 2′—minimum values of losses for #1 and #2 a-C:H(Co) covers, which are obtained by the 90° turning of covers relative to the position on the microstrip, where the maximum values of losses are observed.

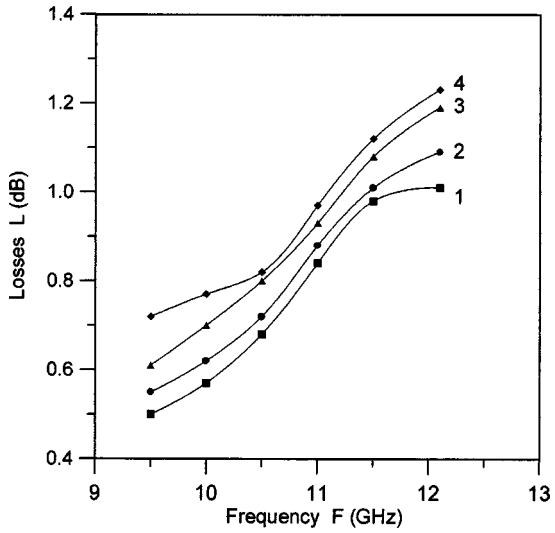

FIG. 5. Frequency dependence of the losses L of normal-incident electromagnetic waves in a-C:H(Co) films sputtered on polycrystal corundum-based substrates. The film thickness and the Co content are: 1—0.77 μm, 20-at. % Co; 2—0.71 μm, 28-at. % Co; 3—0.8 μm, 36-at. % Co; 4—0.81 μm, 43-at. % Co.

plained in the following way: The self-consistent field H_s acting on particles is the sum of an exchange field and the field H_i. The exchange field is determined by the exchange interaction between d-electron spins of Co particles and spins of unpaired localized electrons of impurities and defects in the amorphous matrix and on particle boundaries. The exchange field should give a greater contribution to the self-consistent field H_s for covers with small particles on corundum-based substrates, in comparison with covers with particles of large sizes on aramide tissues. The particles are in potential minima when the self-consistent field H_s has positive sign. At the same time, the magnetic field H_i can have a negative sign, and the spin orientations of particles and the inner magnetic field H_i can be opposite. In all probability, this is realized in a-C:H(Co) covers with small Co particles on corundum-based substrates, where the exchange field has higher values. This supposition have to be studied in more detail in the next experiments.

Figure 4 shows frequency dependencies of maximum and minimum values of losses of the electromagnetic mode propagated along the microstrip line for two samples of a-C:H(Co) covers on aramide tissues. Maximum values are obtained when a-C:H(Co) covers are placed on the position on the microstrip which is the result of the 90° turning relative to the position, where minimum values of losses are observed. This anisotropy of losses is not observed in a-C:H(Co) samples on corundum-based substrates. The effect of the loss anisotropy in covers on aramide tissues can be caused by the magnetic anisotropy of Co particles that originated from the hcp structure. If sizes of Co particles are small (less than 22–24 nm), the cobalt is in the fcc phase. For Co particles with sizes greater than 24 nm, the hcp phase is observed. The a-C:H(Co) films on corundum-based substrates contain Co particles with average sizes of 2.2–3.5 nm.[4] The sizes of Co particles in a-C:H(Co) covers on aramide tissues are in the range of 80–800 nm. Therefore, Co particles in covers on aramide tissues should have the magnetic anisotropy caused by the hcp phase. In the case when axes of the magnetic anisotropy of particles have preferred orientation along a certain direction in the tissue area, the magnetic permeability should have the anisotropy and we can observe the anisotropy of losses. Contributions of the magnetic anisotropy of Co particles to the anisotropy of losses have to be studied in more detail in the next experiments.

IV. ABSORPTION OF NORMAL-INCIDENT ELECTROMAGNETIC WAVES

The losses of normal-incident electromagnetic waves in a-C:H(Co) covers were carried out by the horn irradiation method in the frequency range of 8–12 GHz. a-C:H(Co) covers were placed on the metal basis. The losses L were defined by relation (1). Frequency dependencies of the losses L of normal-incident waves in a-C:H(Co) films sputtered on polycrystal corundum-based substrates are presented in Fig. 5. The films with closely equal thicknesses have different Co concentrations and have a cluster structure below the percolation threshold. It can be seen that the losses L grow with the increasing concentration of cobalt nanoparticles. Maximum values of losses are observed for films with Co concentration in the percolation threshold region (50–60 at. %). A further increase of the Co concentration leads to a sharp change in the conductivity and in the value of the wave impedance of the cover

$$Z = \left(\frac{\mu' + i\mu''}{\varepsilon' + i\varepsilon''} \right)^{1/2}.$$

If the Co concentration is high (>60 at. %), so that the film structure is above the percolation threshold region, a-C:H(Co) covers have very high conductivity and become

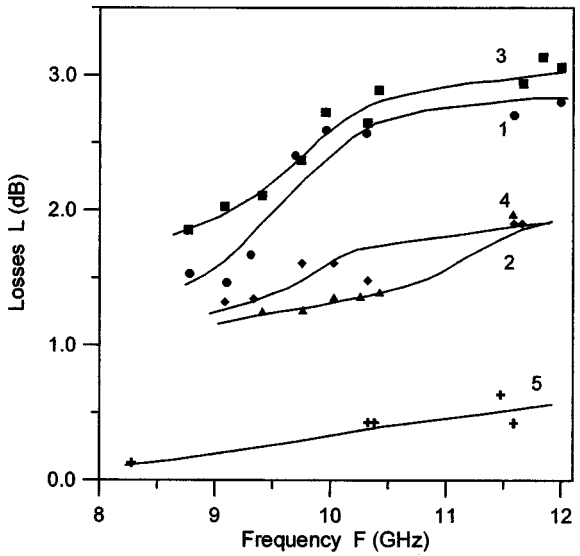

FIG. 6. Frequency dependence of the losses L of normal-incident electromagnetic waves in four-layer a-C:H(Co) covers on aramide tissues. The a-C:H(Co) film thickness on aramide filaments and the Co content are: 1—0.95 μm, 45-at. % Co; 2—0.95 μm, 39-at. % Co; 3—2.1 μm, 39-at. % Co; 4—1.05 μm, 32-at. % Co; 5—four layers of the aramide tissue without a-C:H(Co) film.

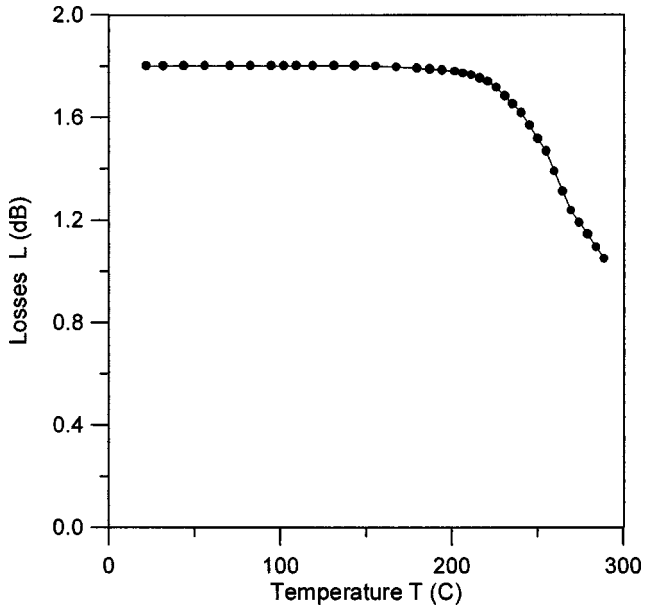

FIG. 7. Temperature dependence of the losses L of normal-incident electromagnetic waves in the four-layer a-C:H(Co) cover on the aramide tissue at a frequency of 9.35 GHz. The a-C:H(Co) film thickness is 0.95 μm; the Co concentration is 45 at. %.

reflective ones. The observed increase in the losses with increasing frequency F in Fig. 5 for films with the Co cluster structure below the percolation threshold can be accounted for by the frequency dependence of the imaginary part of the magnetic permeability μ''.[2,3] The imaginary part of the magnetic permeability grows due to the fast spin-polarized relaxation of Co d-electron spins, which increases with increasing frequency.[1,2] The maximum of losses-per-cover-thickness unit is observed for covers with 43-at. % Co and is equal to 1.5 dB/μm at the frequency $F=12$ GHz.

Figure 6 shows the frequency dependencies of the losses of normal-incident electromagnetic waves in a-C:H(Co) covers with the cobalt cluster structure below the percolation threshold on aramide tissues. Each cover consists of four a-C:H(Co) layers. The losses L grow with increasing Co concentration. For the covers studied, the additive effect is revealed—the losses L grow proportionally with the increase in thickness of the a-C:H(Co) film on aramide filaments. The maximum of losses-per-cover-thickness unit is observed for covers with 45-at. % Co and reaches up to 0.73 dB/μm at the frequency $F=12$ GHz. This value is lower than the value of losses per thickness for covers on corundum-based substrates.

The temperature dependence of the losses of normal-incident waves in the a-C:H(Co) cover contained four layers on the aramide tissue is presented in Fig. 7. Each cover has a-C:H(Co) films on aramide filaments with a thickness of 0.95 μm and a Co concentration of 45 at. %. The experiment was carried out at a frequency of 9.35 GHz. The values of the losses L vary by a small amount up to the temperature 230 °C. In the temperature range of 230–280 °C hydrogen is left from a-C:H(Co) films. This leads to the graphitization of the cover and increases in the conductivity. Under these conditions, the reflectivity of the cover grows and the losses L decrease.

V. CONCLUSION

We have investigated the losses of microwave electromagnetic radiation in granular structures of amorphous hydrogenated carbon with Co nanoparticles a-C:H(Co) and obtained the following results:

(1) a-C:H(Co) films sputtered on corundum-based substrates have higher losses than do films with the same thickness and Co content sputtered on aramide tissues. The difference between the losses is accounted for by the difference in localization sizes of cluster electron states in a-C:H(Co) films.
(2) If the a-C:H(Co) film structure is below the percolation threshold, the losses grow with increasing concentration of cobalt nanoparticles. Maximum values of losses are observed for films with Co concentration in the percolation threshold region.
(3) The observed increase in the losses with increasing frequency is accounted for by the growth of the imaginary part of the magnetic permeability due to the fast spin-polarized relaxation of Co d-electron spins.
(4) The anisotropy of losses in a-C:H(Co) covers on aramide tissues is observed. We suppose that the effect of the anisotropy of losses can be caused by the magnetic anisotropy of Co particles that originated from the hcp structure.

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