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Electromagnetic Characterization of NAnostructured Materials

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Recommendations and validity domains of techniques for experimental electromagnetic characterization of different nanostructured materials based on their chemical and geometrical structures

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1 Introduction: Existing techniques for electromagnetic characterization and their application to nanostructured materials

The electromagnetic characterization of nanostructured materials is a very difficult problem even for a specialist in the electromagnetic theory. As it was shown in our reports [1, 2, 3, 4] the situation in the electromagnetic characterization of nanostructured materials is not favorable for the choice of the best technique if the material is resonant (then it is called metamaterial). First, among the methods of the electromagnetic characterization of nanostructured materials only two methods - Nicolson-Ross-Weir (NRW) retrieval [5, 6] and Variable-Angle-Spectroscopic-Ellipsometry (VASE) retrieval [7, 8] - have been developed enough to be supported by ready numerical and experimental techniques. These techniques deliver more reliable results than the conventional ellipsometry and spectroscopy which have been used for the ages to characterize natural materials. Conventional methods imply the variety of differently shaped samples of the same material and cannot give reliable results for artificial media which are usually prepared as layers grown or printed on a wafer or another substrate.

The NRW method is based on the measurement of the complex refraction R and transmission T coefficients for a normally incident plane wave (i.e. includes the reflection and transmission phase measurements). It is used to characterize bulk magnetoelectric layers including thin films in the radio frequency range. With respect to nanostructured materials whose electromagnetic properties refer to the optical region, this method can be reduced to the measurement of only absolute values of R and T or to the measurement of only complex R. This becomes possible because permeability μ of usual materials in the optical frequency region is equal to 1, and to retrieve two real values, namely real and imaginary parts of the medium permittivity ε is possible from two measured values. In this variant the NRW method (namely, the Schopper technique and the Malé technique [9]) had existed earlier than different techniques of the NRW method were developed by microwave engineers for magneto-dielectrics. The NRW method gives not a full characterization of anisotropic material since is restricted by the normal incidence only. Below some additional information on the NRW method is presented.

The VASE method is combination of the ellipsometry and spectroscopy and is applicable to characterize layers of anisotropic (uniaxial) media whose complex permittivity is a tensor. It gives the better accuracy for nanostructured thin films than the NRW method especially in the case of losses. Below some additional information on the VASE technique is presented.

The literature analysis in our reports [1, 2, 3, 4] clearly showed that these two well-developed methods are suitable only for those nanostructured materials whose nanosized elements are optically densely packed and not resonant. These two methods are not applicable to nanostructured photonic crystals, nanopatterned diffraction gratings. Such optically sparse structures cannot be characterized in terms of few material parameters [1]. These two methods are also not applicable to nanostructured metamaterials, i.e. composites with optically dense package of *resonant* constitutive nanoelements. Nanostructured metamaterials form an important class of artificial materials, as it is clear from the classification [1]. For the characterization of nanostructured metamaterials more advanced methods are needed.

However, these more advanced methods, whose overviews were presented in [1, 2, 3, 4], are currently under theoretical study and cannot be referred to as real techniques. Therefore in this report we omit these prospective advanced methods and consider limitations to the existing techniques related to the structural and chemical properties of nanostructured materials.

In fact the application of existing NRW and VASE techniques for bulk nanostrucrtured materials is justified if the researcher understands that these methods deliver wrong numerical data for resonant materials. These two methods allow one to partially analyze the dispersion of the material in the broad band. Even if the retrieved dispersion curves violate the physical limitations listed in [4] they allow one to judge on the presence of the resonance of constitutive elements. Moreover, they correctly share out the resonance frequency band [15] i.e. allow one to compare the experimental resonant frequency with that predicted theoretically. Beyond the resonance band there is no difference between metamaterials and usual materials for which these two methods are applicable. Therefore both these techniques in absence of the better alternative are recommended to apply for bulk nanostructured materials. The general condition of their application for the quantitative characterization of such materials should be respected: the material should satisfy to the limitations of bulk effectively continuous non-resonant passive medium. In other words, in the frequency region for which the characterization is to be done

- the arrangement of inclusions should be optically dense;
- should be optically small;
- inclusions should not be arranged in chiral and magnetic arrays;
- the material layer thickness should be significantly larger than the inclusion sizes;
- concentration of inclusions should not strongly vary in the illuminated spatial domain;
- inclusions should be passive (no generation in then);
- inclusions should be non-resonant.

For a qualitative characterization (resonance band) one can apply these methods even if the last condition is not respected (but not the others). To experimentally check all these conditions except two last ones it is possible using the structural characterization. The last conditions can be experimentally estimated using the chemical characterization.

Structural characterization is obvious for nanostructured materials. First, it allows one to check is the arrangement of material nanoelements optically dense and regular. If particles are too large or distanced from one another to the distance comparable to the wavelength one should expect the spatial dispersion effects. For example, if the particle size or interparticle distance exceed half-wavelength, at this wavelength the nanostructure will strongly scatter and it is useless to c characterize it in terms of material parameters. If the optically sparse structure is regular it will behave as a diffraction grid if it is a surface structure. It will behave as a photonic crystal if it is bulk. Second, structural characterization allows one to see the presence or absence of asymmetry of structural elements and their arrangement. For example, if these elements are springs the array of these elements must possess chirality. If these elements are simple-shape nanoparticles arranged so that they form nanostructured helices, the material will be chiral again. Such a material cannot be described by a homogeneous permittivity, the chirality material parameter needs to be introduced. If particles form effective loops one can expect the artificial magnetism.

We can see that one needs to make the structural (and desirably chemical) characterization together with the experimental electromagnetic characterization or even prior to it. Only if the structure is really what we theoretically expect we can compare the theoretical and experimental data. Otherwise, we have to eliminate the factors, which disturb the experimental

characterization process, for example to remake the sample, or to elaborate the theoretical model, introducing the factors we observed after the structural and chemical characterization.

Chemical characterization methods of nanostructured materials are described e.g. in the overview paper [22] and book [23]. It allows one to check the presence or absence of constitutive elements which can be responsible for interesting and advantageous properties, such as plasmonic or refractory metals, semiconductor crystalline media, heterostructures, etc. In the next section we give a brief review of the structural characterization methods.

2 Retrieval of material parameters for non-resonant nanostructures

2.1 Nicolson-Ross-Weir retrieval

NRW retrieval method is based on the inversion of the Fresnel-Airy formulas expressing the normal reflection and transmission coefficients of a material layer through the wave impedance of the medium and its refraction index. Through the wave impedance and the refraction index one can find medium permittivity and permeability (for anisotropic media – tangential components of the permittivity and permeability tensors).

Under the alternative name of the distributed impedance method the NRW method is known in both numerical and experimental characterization of natural materials [5, 6] as well as of composite (granular) materials with very optically dense arrangement of grains [10, 11]. However in these works only non-resonant grains were considered. As it was theoretically shown in works [12, 13, 14, 15] and experimentally confirmed in [16] this technique is not applicable when the sample material experiences the resonance. Another limitation of this method is poor resolution for losses [5]. The advantage is broadband description of the dielectric (and non-resonant magnetic) properties [10].

In the NRW method the transmission and reflection signals are tested to calculate the dielectric properties of the layer. In the microwave frequency range one uses network analyzers which combine the tester and signal source [5, 10]. In the optical frequency range the reflected signal amplitude should be measured by a spectroscope. To spatially separate the reflected wave from the incident one one commonly uses in optical measurements the semi-transparent mirror which is tilted under the angle 45° to the incident wave (see e.g. [17]). The phase of the optical signal is measured using the Mach-Zender interferometer (see e.g. [18]). Since non-resonant bulk nanostructures do not possess magnetic permeability in the optical range the interferometric measurements can be avoided. The complex permittivity (real and imaginary part) of the dielectric layer or film can be retrieved only from spectroscopic measurements, i.e. from $|R|$ and $|T|$ [9]. However, the film is always prepared on the substrate which ensures the mechanical robustness of the film. Therefore the retrieval procedure obviously takes into account the permittivity of the substrate [9]. For nanofilms obtained by epitaxial or lithographic methods it is not a problem since the permittivity of the substrate does not change after the fabrication of the film. However, many nanostructured materials are chemically grown on the substrate and the fabrication process is related with high temperatures. Then the substrate permittivity will be slightly modified. Since the substrate is always optically thick this slight modification leads to a serious mistake in the transmittance $|T|$ calculated for a non-perturbed substrate. In this case a more accurate experimental retrieval of complex permittivity is achieved by the measurements of $|R|$ (spectroscopic) and $phase(R)$ (interferometric) [18].

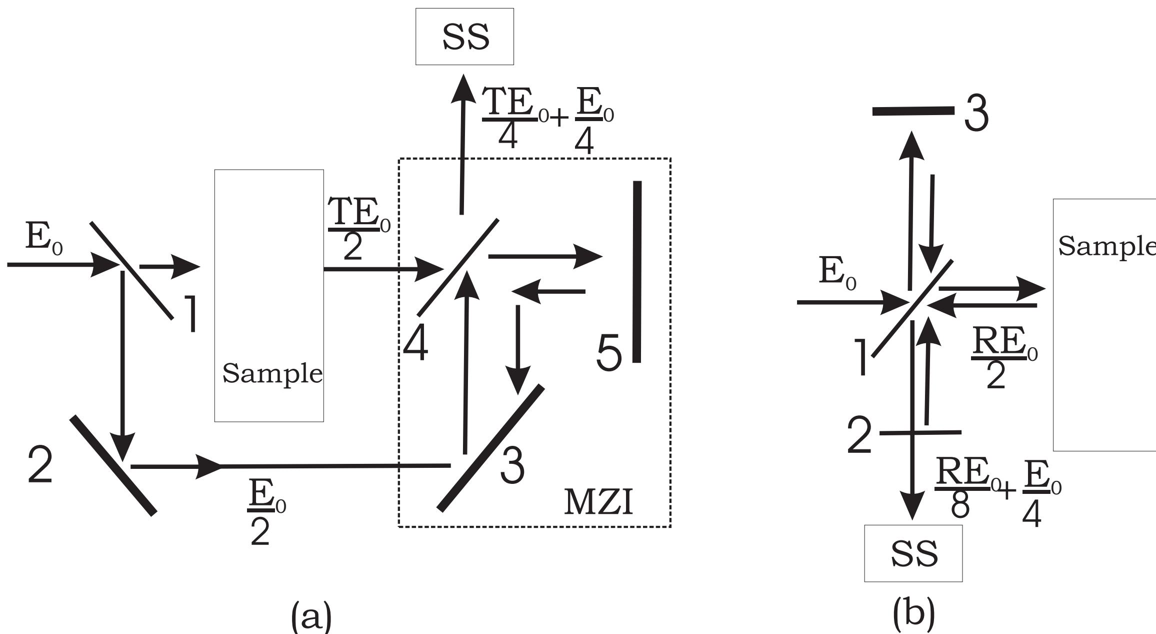

Figure 1: The configurations used in the NRW method at optical frequencies. (a)– Measurements of the amplitude and phase of the transmission coefficient T. The amplitude of T is measured by a spectroscope (SS). The spectroscope signal contains also a 1/4 part of the incident wave. Since the optical path of this part is known this parasitic signal can be eliminated by an additional branch (not shown) which adds the signal $E_0/4$ with the opposite phase. Alternatively, this can be taken into account in the software. Semitransparent mirror 1 is needed to split the incident beam to that illuminating the sample and that used for the measurement of the phase. Semitransparent mirror 4 is needed to split the transmitted beam to that directed to SS and that used in the phase measurement. The phase is measured by the Mach-Zender Interferometer (MZI) formed by fully reflecting mirrors 3 and 5 with the help of semitransparent mirror 4. (b) – Measurements of the amplitude and phase of the reflection coefficient R. The amplitude of T is measured by a spectroscope (SS) whereas semitransparent mirror 1 is used to split the incident beam. This spectroscope signal contains the known parasitic part to be compensated. The MZI is formed by semitransparent mirror 2 and fully reflecting mirror 3.

The NRW technique is more troublesome at optical frequencies than at microwaves as difficult and precise phase measurements must be taken from the signal. This is achieved through the use of a Mach-Zender interferometer which splits the beam into two (one wave passes through the sample, the other is used as a reference) before each being picked up by a detector [43]. The measurement schemes are rather cumbersome as one can see in Fig. 1. In the transmission scheme the spectroscopic device SS measures the signal with absolute value of the complex amplitude $|E_0(T+1)/4|$ and the Mach-Zender interferometer (MZI) measures the phase shift between two signals, one has the complex amplitude $E_0T/4$ and another – $E_0/4$. From these data one extracts the amplitude and phase of T. In the reflection scheme SS measures $|E_0(R+1)/4|$ and the MZI measures the phase shift between signals $E_0R/8$ and $E_0/2$.

In fact, interferometric measurements need not be taken with non-resonant bulk nanostructures as they do not exhibit magnetic permeability at optical frequencies. The natural magnetism in the optical range is absent, only resonant structures demonstrate the artificial

magnetism. To extract complex permittivity it is sufficient to measure two real values – $|R|$ and $|T|$.

It should always be remembered that the thin nanofilm or dielectric being characterized sits atop of an optically thick substrate. Thus, the substrate too should be measured. The values retrieved for both the real and imaginary parts of the permittivity are influenced by some degree by the sample substrate [44], the extent of which is dependent on the fabrication process used to create the nanofilm. If epitaxial or lithographic techniques are used the effect will be non-existent because the substrate permittivity will remain the same after the fabrication of the nanostructure. If the nanostructured materials are however fabricated using chemical growth, a process that crucially involves the sample being subjected to high temperatures, the substrate permittivity will be irreparably altered. The effects of this modification will be augmented by the fact that the substrate is comparatively thick in size. Consequently when the transmittance coefficients are measured they and the material parameters calculated using them will be completely incorrect for a non-perturbed substrate. An alternative method in this instance would be retrieval of parameters using both the spectroscopic and interferometric reflectance [43].

Let us conclude this subsection by three important comments. The NRW method implies the normal propagation of the wave in the material. Therefore, the obvious condition of optical smallness of the structure period a refers only to the period across the slab. To consider the medium as effectively continuous is possible not only if the slab is formed by optically small inclusions. It can be an array of long inclusions (e.g. wires) if they are parallel to the boundary. This possibility seems to broaden the scope of applicability for this method. However, it is not so simple. In fact, the retrieved effective material parameters can be treated as characteristic parameters only in the case when the particles are optically small and isotropic. Then once retrieved from the measurements of r and t coefficients for the normal incidence they can be applied for condensed description of the materials. For a slab of the wire medium or for a structure of alternating metal and dielectric layers it is not so. In them the oblique propagation obeys to different laws than the normal propagation. The interaction of the obliquely propagating wave with such media cannot be considered in terms of the permittivity which was retrieved for the normal incidence. Moreover, in the case of the oblique propagation of the wave such media are spatially dispersive and to relate their effective material parameters to r and t coefficients so-called additional boundary conditions are needed (see e.g. in [41]). However, if there is a reliable theoretical model of the structure and a minimal knowledge on its geometrical parameters (e.g. the period a across the slab) the NRW retrieval will be not useless. For example, for a wire medium from the retrieved permittivity one can find the so-called plasma frequency which can be further used for calculating the spatially dispersive material parameters. This case can be referred as partial or conditional electromagnetic characterization.

The second comment refers to the obvious condition of the absence of the resonances. In fact, the NRW method is applicable beyond the frequency range of the Fabry-Pérot resonances (thickness resonances of the slab) [40]. At these resonances the method if applied leads to the violation of physical laws in the retrieved material parameters.

The third comment is about the NRW retrieval in comparison with the alternative approach to the material parameters retrieval, i.e. the ellipsometric methods. The drawback of the NRW method is that it does not have a sufficient resolution to measure low loss tangents [45]. Its main advantage is that can be applied in a wide frequency range where provides the broadband description of the medium dispersive properties.

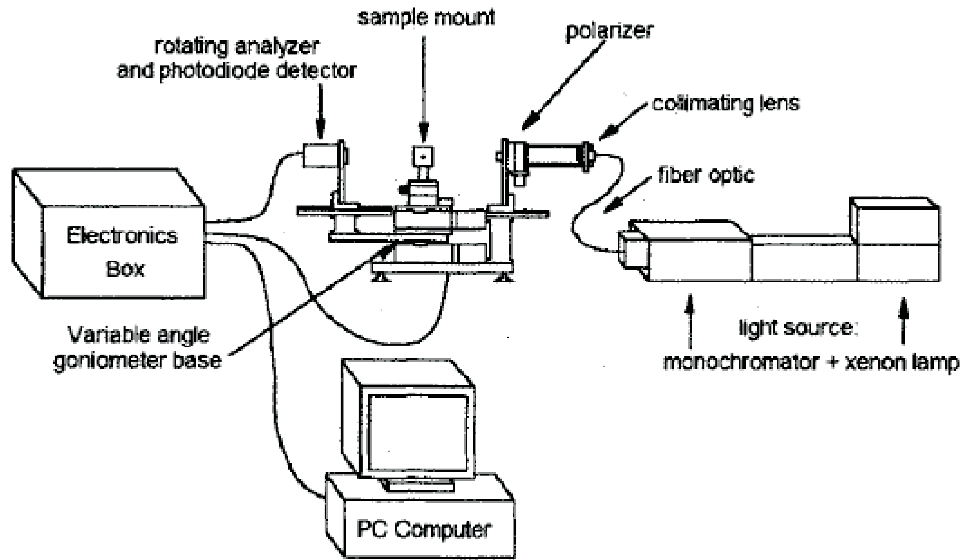

Figure 2: A block diagram of a VASE retrieval system in the Rotating Analyser Ellipsometer (RAE) configuration [48]

2.2 VASE retrieval

Between known ellipsometric methods the so-called Variable Angle Spectroscopic Ellipsometry (VASE) [46, 47] has been recently recognized as most useful and highly accurate method of calculating material parameters from the data of optical measurements. Whilst it does not directly measure the complex permittivity, the mathematical model it uses to deduce this and other such parameters gives a precise and reliable output without the need for referential measurements. Standard spectroscopic ellipsometry methods measure the Fresnel reflection coefficients as a function of wavelength only. Where VASE retrieval differs is that it measures the sample's coefficients in s- and p- polarized light (where s- is electric field perpendicular to and p- is in to the plane of incidence) as a function of wavelength and angle of incidence [48]. Measurements are obtained using several incident angles of light which results in an improvement in sensitivity and precision because the received data is taken using a variety of optical path lengths. Light is first passed through a monochromator to narrow its spectral band to a desired range before passing through a polarizer. It then strikes the specimen at an oblique angle, reflects onto a second, sometimes rotating polarizer known as an analyzer and is received by a detector. The angle of incidence, which is controlled by computer, generally varies between 50° and 80° in a rotating analyzer ellipsometer (RAE, shown in Figure 2) but this is dependent on the sample type [48].

Variable Angle Spectroscopic Ellipsometer [7, 8] is an excellent tool to indirectly measure the complex permittivity of a layer with both known and unknown thickness. For the case when the layer thickness is known VASE instruments can measure the complex permittivity of a uniaxially anisotropic layers. Since a nanostructured layer must be previously geometrically characterized and its thickness should be already known, this review is concentrate on the possibility to measure both components of the permittivity tensor.

The VASE setup shines linearly polarized light on the sample surface with different angles of incidence. The electric field vector is oriented obliquely with respect to the plane of

the light incidence. Then the ellipticity of the reflected light from the sample surface (which obviously appears in the case of the oblique incidence as one can see from the Fresnel-Airy formulas) is analyzed for the s-polarized component of the electric field vector (component in the plane of incidence) and p-polarized component (that orthogonal to the incidence plane). The spectrometer measures the ratio of the s and p components for different angles and the existing softwares [19] fit the angular dependence of these results to the mathematically generated model of this angular dependence expected for a uniaxial layer of given thickness. This fitting delivers the most suitable values of both components of the complex permittivity tensor at a given wavelength. Since the data is measured over the entire wavelength range the analysis of the frequency dispersion of the permittivity allows one to judge on the applicability of the VASE technique to the given nanostructure. If the dispersion turns out to be non-physical, i.e. violates physical limitations [4], the method is not applicable. For natural films it was checked that the VASE retrieval is very accurate even near the absorption peaks where the dispersion of permittivity appears [20]. Therefore it should be applicable also for electromagnetic characterization of isotropic and uniaxial nanostructured layers beyond the resonance of its constitutive elements. Instructions of the usage can be found in the Internet [21].

There are numerous configurations available for variable angle ellipsometers, each with their own advantages, disadvantages and range of optimal incident angles. These are detailed in the literature. The resultant ratio of s and p reflectance coefficients is calculated for each angle and then compared with an assumed mathematical model detailing the physical structure of the specimen. The mathematical model of the oblique reflection of the wave from a layer of anisotropic medium with unknown tensor permittivity located on a known substrate is then used to derive the unknown permittivity. Although this overview is primarily interested in optical parameters, the layer thickness and surface and layer junction roughness can also be obtained using VASE retrieval. The high sensitivity and consequent high accuracy of VASE retrieval techniques are their strongest advantage. Their ability to be constructed in a variety of configurations also means that the system can be setup and used in a way that is optimal for each sample being tested. However care must be taken to ensure that the nanostructure under examination is suitable for VASE retrieval. Because measurements are performed using a large wavelength range the suitability of a nanostructure must be scrutinized by analyzing the frequency dispersion of the permittivity. Samples that produce non-physical dispersion that defy tangible limitations are not suitable for VASE retrieval techniques.

3 Structural characterization

3.1 Atomic force microscopy

Atomic force microscopy AFM) also known as scanning force microscopy(SFM) is a basic technique for the analysis of nanostructured surfaces and AFM are inevitable in all nanoscopic research. Like all other scanning probe microscopies (SPM), AFM works by scanning with a tip (or more general a probe) very close to the sample surface. It operates by measuring attractive or repulsive forces between the tip and the sample in constant height or constant force mode. Most spectacular are atomic resolution and atomic manipulation, but most practical applications deal with the sub-micrometer (¿100 nm) x/y-range and nanovertical (nano-z) range. The best resolution for vibrational AFM has been achieved to present time by so-called shear-force AFM with horizontal tip vibration (1 nm in the vertical direction and 10 nm is

the horizontal one) [24]. The resolution in the vertical direction here is much higher than that achieved with a modern immersion optical microscope (200 nm in the violet range) and is higher than that of a aperture near-field scanning microscope (20 nm). The three-dimensional information is another most important distinguishing feature of AFM. It supplements electron microscopy and increases the possibilities, as it does not require surface treatment obvious for SEM and TEM and is able to measure at ambient conditions. Unlike scanning tunneling microscopy (STM) the samples need not be electrically conductive.

Other surface properties such as friction forces, sample elasticity, adhesion, or chemical differences by lateral and torsional force sensing, force modulation, frequency modulation, and phase imaging are available. Magnetic nanostructures are scanned by special type of AFM called magnetic force microscopes (MFM) using cantilever tips that are coated with a ferromagnetic film of a few nm thickness. Most applications of MFM are in the storage media industry. Virtually all solid surfaces from all branches of science, industry, medicine, daily life are, thus, accessible to nanoscopic investigation with unprecedent information. The details how to apply AFM and interpret AFM images can be found in the handbook [24].

3.2 Near-field optical microscopy

Another type of scanning microscopy if near-field optical microscopy (SNOM). It is a microscopic technique for nanostructure investigation that breaks the far field resolution limit exploiting the properties of evanescent waves. As in the case of AFM it is achieved by price of a rather long scanning process. The image of the nanosized domain of the surface is done by placing the detector very close (distance much smaller than wavelength) to the specimen surface. This allows for the surface inspection with high spatial, spectral and temporal resolving power. In particular, lateral resolution of 20 nm and vertical resolution of 25 nm have been demonstrated [25]. As in optical microscopy, the contrast mechanism can be easily adapted to study different properties, such as refractive index, chemical structure and local stress. Dynamic properties can also be studied at a sub-wavelength scale using this method. The main drawback of SNOM compared to AFM is the fragility of the nanometer thick part (tip) of their cantilever because they are either prepared of a dielectric or semiconductor material transparent for light. Sometimes the tips are covered with metal film which enhances the resolution but does not change the mechanical robustness. Another drawback of SNOM is less resolution that that of best AFM (see above). However SNOM are usually cheaper than AFM and therefore stand the contest with AFM [24].

3.3 Electron microscopy

Electron microscopy [26] differs from AFM and SNOM by possibility to give images of the structure bulk since electrons penetrate deeply under the surface. This is a type of microscope that produces an electronically-magnified image of a specimen for most detailed observation. The electron microscope (EM) uses a particle beam of electrons illuminating the specimen and creating a magnified image of it. The magnification of scanning electron microscope (SEM) and transmission electron microscope (TEM) achieves $2 \cdot 10^6$. The resolution is also not achievable for AFM and SNOM. Resolution of the modern TEM called High Resolution TEM is not limited by spherical aberration and is equal to 0.5 Angstr om (0.05 nm) [26]. The drawback of TEM compared to SEM is the applicability to characterize mainly surface structures because the image is created by the diffraction of electrons at the surface.

The SEM produces images by probing the specimen with a focused electron beam that is scanned across a rectangular area of the specimen (raster scanning). At each point on the specimen the incident electron beam loses some energy, and that lost energy is converted into other forms, such as heat, emission of low-energy secondary electrons, light emission (cathode-luminescence) or x-ray emission. The display of the SEM maps the varying intensity of any of these signals into the image in a position corresponding to the position of the beam on the specimen when the signal was generated. Generally, the image resolution of an SEM is about 10 times poorer than that of a TEM. However, because the SEM image relies on surface processes instead of the diffraction of transmitted electron beams, it is able to image bulk samples up to many centimeters in size and depending on instrument design and settings has a great depth of field. So, it can produce images that are good representations of the three-dimensional shape of the sample [26].

There are also other types of EM such as reflection EM, scanning-and-transmission EM, etc. They all have common drawbacks. All electron microscopes are expensive (also expensive to maintain compared to AFM and SNOM). They are dynamic rather than static in their operation, requiring extremely stable high-voltage supplies, extremely stable currents to electromagnetic lenses, continuously-pumped high- or ultra-high-vacuum systems, and a cooling water supply circulation through the lenses and pumps. As they are very sensitive to vibration and external magnetic fields, microscopes designed to achieve high resolutions must be housed in stable buildings (sometimes underground) with special services such as natural magnetic field cancelling systems [26].

Some modern EM are relatively inexpensive. These EM are low voltage electron microscopes with TEM capabilities at 5-10 kV without stringent voltage supply, lens coil current, cooling water or vibration isolation requirements. These EM are far easier to install and maintain, but their resolution does not differ very much from that of best AFM having practically the same price. As a rule EM requires that the sample is placed in vacuum, as the molecules that make up air would scatter the electrons. One exception is the environmental scanning electron microscope, which allows hydrated samples to be viewed in a low-pressure wet environment [26].

4 Restrictions in the electromagnetic characterization of nanostructured materials

4.1 Geometrical restrictions

Metal nanoparticles are the most popular constitutive elements of nanostructured metamaterials operating in the optical frequency range. It is so because the ratio size/wavelength at the plasmon resonance can be very small which creates good presuppositions for the homogenization of a material and, consequently, its description in terms of effective material parameters (EMP). However, the minimal ratio size/wavelength is still restricted. This results from an important quantum effect: the weak localization of conduction electrons at the surface of the metal nanoparticles [27, 28]. Due to this restriction macroscopic parameters such as complex permittivity and complex conductivity (usually uniquely related with one another) cannot be introduced in the usual way for particles whose minimal size is less than 5-6 nm [28, 29]. In principle, one still can describe the electromagnetic response of metal particles with sizes with the interval 1-6 nm through complex permittivity or complex conductivity, however these pa-

rameters are mesoscopic and can be found only after a special quantum modelling [30]. In any case these parameters do not obey the Drude dispersion law whereas larger metal nanoparticles do [29, 30]. Furthermore, the strong confinement of conductivity electrons at the surface of so small nanoparticles leads to the significant increase of their losses and damages the plasmon resonance. Therefore, so small particles are not so promising for obtaining metamaterials as particles larger than 5-6 nm.

Metal particles with sizes less than 1 nm cannot be described through own permittivity or conductivity and their properties are different from those of samples of bulk metals [31]. Such small ensembles of atoms possess certain regularity but are not yet crystal lattices. These are only embryos of the metallic state. Depending on the host medium such sub-nanoparticles can be attributed to conductors or insulators [32]. Optical properties, especially non-linear ones, such as fluorescence, luminescence, higher harmonics generation, etc. are also mesoscopic and dependent on the background [33]. It is difficult to characterize them theoretically. Of course, in principle one can find dipole polarizabilities of metal sub-nanosized particles, and these polarizabilities are also resonant in the optical range (though their resonance cannot be called as plasmon one). However, the threshold of their non-linearity is strongly lower than that of bigger (crystalline) nanoparticles.

Respectively, it is difficult to retrieve linear EMP of arrays of sub-nanosized metal particles. To ensure the linear regime one needs low fields, however the strong absorption of these field will lead to the very low level of the transmitted field which will hardly allow one to measure the transmission phase. Composites of metal particles with sizes less than 1 nm [31, 32, 33] are exotic metamaterials, for which no methods of electromagnetic characterization are available in the accessible literature. Composites (including lattices) of metal particles whose size is between 1 and 6 nm can be characterized in terms of EMP, however due to strong absorption in such structures it is still difficult to measure the transmission phase in them [34]. Therefore researches working with such composite concentrate on the spectroscopic studies [35]. From spectroscopic data under certain assumption one can find the complex permittivity as it is done in classical optics [37, 38]. The main assumption in this quasi-static characterization procedure is the absence of magnetic properties and of spatial dispersion which opens the door to the use of Kramers-Kronig relations. Another assumption is the absence of Drude transition layers which as it was explained in our previous reports implies the negligible phase shift per unit cell of the composite medium. In [36] one presented a structure in which the touching gold nanoparticles of diameter 2 nm form nanochains of length few tens nm in liquid crystal matrices are not studied even theoretically. Properties of such a nanochain are not yet studied even theoretically. Since the dissipation level in such nanochains has not been estimated, it is not clear (for the instance) can the NRW method or any other phase method be applied with practical accuracy for the electromagnetic characterization of such metamaterials or not.

Notice, that the weak localization of plasmonic electrons makes difficult the description of clusters of metal nanoparticles. It becomes impossible in terms of classical electrodynamics if the distance between metal nanoparticles in a cluster is between 0.01 nm and 1 nm [32]. Then the tunnel effect is strong and the quantum model should be developed for the whole cluster. The description of the cluster in terms of the permittivity is probably possible but is a challenging task. This permittivity will be, of course, strongly mesoscopic [39]. The distance between nanoparticles less than one tenth of Angström is equivalent to their direct contact [31]. Such a nanopair or a nanocluster (e.g. a nanochain mentioned above) can be considered as a complex shape nanoparticle, and its internal complex permittivity can be introduced in a quasi-classical way [49, 50].

Semiconductor nanoparticles can be described through internal complex permittivity (that of the corresponding bulk medium) only in the amorphous state. In the crystal state a semiconductor nanoparticle is an Ekimov-Onushchenko quantum dot [51] and the description in terms of the internal permittivity becomes difficult. First, permittivity as such cannot describe the size-sensitive quantization (the basic physical effect responsible for the coherent light generation and fluorescence in quantum dots). Therefore an attempt to describe an Ekimov-Onushchenko quantum dot excited by the light at its eigenfrequencies or excited by the intensive light in terms of the permittivity would be completely inadequate [52]. This assertion refers also to the permittivity with the inverse sign of the imaginary part as it is adopted for the active medium in the laser theory, since the radiation of a quantum dot has totally different nature. Second, the non-linearity of a quantum dot in the whole optical range is very strong and can hardly be neglected even if the light intensity is not sufficient for pumping and the frequencies are far from the nanocrystal eigenfrequencies [53]. Arrays of semiconductor nanocrystals cannot be then characterized in terms of bulk EMP.

To sum up: theoretical electromagnetic characterization of bulk nanostructured materials implies that the permittivity of their constituents is known and can be taken from the available literature, but it is not always so. The most important restriction is related with the size of metal nanoparticles and the distance between them. Both of them should not be less than 1-2 nm, otherwise it is practically impossible to theoretically calculate EMP of the whole material. As to the calculation of material parameters for material with sub-nm inclusions, it is in principle possible, however, one has to exclude the nonlinear effects. For material including such inherently nonlinear structures as quantum dots the possibility to characterize them by usual material parameters seems to be doubtful. No physically sound results of such calculations were found in the available literature.

4.2 Chemical restrictions

The methods of nanofabrication split to physical and chemical ones [54]. There are also combined physical-chemical nanotechnologies, for example nano-imprint lithography including plasma-enhanced chemical vapor deposition [55]. Chemical technologies are mainly associated with self-assembly of nanostructures.

The typical consequence of the self-assembly of nanoparticle arrays is the adhesion of molecules (e.g. organic ones as in [36]) on the particles surface. This process is important for the robustness of nanochains obtained in [36]. However, the mesosopic shield formed by these molecules changes drastically the electromagnetic properties of nanoparticles. For example, it leads to a shift of the plasmon resonance frequency and to a reduction of the resonance magnitude [58]. This effect is significant for organic molecules. Therefore if organic molecules are present the shift of the plasmon resonance with respect to the theoretical predictions must be expected. For media of semiconducting nanocrystals (e.g. arrays of quantum dots) the covering with organic or hydrophobic molecules is very important since preserves the quality of the crystal. Otherwise the regularity of the crystal lattice of semiconductor is very soon destroyed by chemically active molecules coming from the host medium [56]. The alternative method to preserve the quantum dots is to immerse them into a chemically inert medium, for example to encapsulate them by a polymer microsphere [57]. To electromagnetically characterize the arrays of quantum dots which are open to the liquid or gas surround is useless.

5 Conclusions

In this report we explained why the structural and perhaps chemical characterizations of nanostructured materials are prerequisites of the electromagnetic one, and indicated in which cases the known techniques of electromagnetic characterization can be applied to such materials. Structural characterization shows the geometrical type of the material and the defects of its fabrication. Also, we can judge on its optical density which is an obvious condition of the description of a material through few material parameters, e.g. complex permittivity and permeability. In the case when a nanostructured material has a nontrivial permeability in the optical range it refers to the class of metamaterials for which the existing techniques are not suitable. However, these methods are not fully useless since they allow one to judge on the resonance of constitutive elements. We considered restrictions to these methods related to sizes of nanoelements, distances between them, shapes and other geometrical issues. Also we indicated restrictions related to the chemical content of the nanomaterial. An overview of the structural characterization methods has been done.

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