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Nanocomposites based on ferroelectrics and meso-systems modified by high-dielectric and high-field environment*

ZHOU Ji (周 济)**

(State Key Laboratory of New Ceramics and Fine Processing, Tsinghua University, Beijing 100084, China)

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Abstract The nanocompoisites of ferroelectric matrix and nanosized particles (clusters) ("ferroelectric-based nanocomposites" for abbreviation) constitute a group of novel functional materials. A new physical system, meso-system modified by high-dielectric and high-field environment, was formed in the composites. These materials show a promising application prospect in nonlinear optics, low driving voltage electroluminescence devices and quantum dot lasers. In this review, the basic design idea and preparation method are introduced; research progress in this area made by the author and other colleagues are summarized; the dielectric and optical properties, the effect of high-dielectric and high-field environment, and the possibility for realizing low driving voltage high-field electroluminescence are reviewed.

Keywords: ferroelectric, nanostructured material, mesosystem, dielectric, electroluminescence devices.

Nanocomposites have been becoming a remarkable hot-point in the research areas of both material science and solid state physics in recent years[1, 2]. Generally, the design of nanocomposites is mainly based on two strategies: (i) the modification of matrix by introducing the nanophase, e.g. the enhancement of turffness of ceramics by introducing metal particles[3]; (ii) using matrices as a holder or host for holding and stabilizing nanophases or for facilitating device manufacturing technique, such as some nonlinear optical clusters embedded in some matrices, e.g. silica glass or zoelites[4, 5]. However, very little work was carried out with the matrix as a supplier of special environment around the nanophases. A new class of composites comprised of ferroelectric matrices and embedded nanoparticles can be classified into this case. As a special multi-functional material, it is a new physical system——meso-system modified by high-dielectric and high-field.

In 1992, the author first proposed the idea of constructing new functional materials and improving some properties of ferroelectrics by means of combining ferroelectrics with metal nanoparticles[6]. Then our primary investigations on the method of synthesis as well as electrical and optical properties were reported and attracted much attention from many colleagues worldwide. Recently we prepared the composites of ferroelectric and C_{60} and that of ferroelectric and semiconductor quantum

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** Permenent address: Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, China.

Current address: Photonics Laborsatory, School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798

Email: ejzhou@ntu.edu.sg

dots. A new concept of meso-system modified by high-dielectric and high-field environment was put forward by us. In this article, we try to summarize and introduce the research idea, main progress and new trends in this area.

1 Main idea of designing ferroelectric based nanocomposites

It is well known that ferroelectrics are a group of special dielectric materials. The main character of them is spontaneous polarization, and the direction of the polarization can be switched by an applied electric field. Because of its special microstructure, ferroelectric materials show many novel physical properties. Commonly, ferroelectrics possess very high dielectric constant (10^3—10^4), high dielectric strengh as well as piezoelectric, pyroelectric, electrooptic and optical nonlinear properties, etc. If nanoparticles or clusters are embedded in a ferroelectric matrix, a series of modification should be imposed on them by the matrix.

(i) Ferroelectric matrix should supply a special environment with a high dielectric constant for the particles, so affects the electric state in the area of interface between the two systems. This should induce a change in the character of electronic state in the nanoparticles, and change the physical properties of the nanoparticles to some extent, and even thoroughly.

(ii) The surrounding ferroelectric matrix should change the surface/interface state of the nanophase, such as increasing the difference of dielectric constants between the two side of the interface or optical diffraction index and interface polarization field. These should induce a change in energy of various excimers, such as suface/interface phonons, surface plasma, and surface/interface excitons, and result in the change of the properties related to the surface/interface.

(iii) A very high local field can be induced inside a solid with a high dielectric constant, so extremely high field can easily be applied on the nanoparticles inside a ferroelectric.

(iv) The phase transition, domain transition, polar reversion and other changes in structure or state in the ferroelectrics can occur with the change of external conditions such as temperature, pressure, electric fields or light irradiation, which would provide a variable physical environment to the nanophase.

It can be seen that there should be a great amount of new physical information and valuable functions contained in the system of ferroelectric-based nanocomposites. This is the main idea for the design of this composite.

2 Preparation method of the composite

A large quantity of embedded nanocomposites with the dielectrics as matrices have been prepared in recent decades. The preparation methods for these materials include sol-gel process[7], glass melting methods[8], radio-frequency sputtering[9] etc. Among them, sol-gel process is the most widely used method. Some simple metal oxides, such as SiO_2, ZrO_2, TiO_2 are selected as the matrices. As these matrix materials are relatively stable chemically and not ready to react with the nanophase, and the precursors for them are easy to be obtained and manipulated, the difficulty for the preparation of these nanocomposites are not big. However, ferroelectrics are different. Firstly, most of them are relatively complex binary- or tertiary-metal oxide, and the precursor of these ferroelectrics tends to react with that of the nanophase. Secondly, to obtain the material with the predicated dielectric properties, a crystallized matrix is required. So, many complex technical issues are involved in the preparation process.

On the basis of a modified sol-gel process of lead zirconate titanate (PZT) thin films, we prepared a composite thin film with PZT matrix and nanoscale Ag particles for the first time in 1992. The main process is that the solution of silver salts was introduced into PZT precursor solution to make silver ions dope into the PZT sol-gel system homogeneously, then the silver ions are reduced into silver atoms and aggregate into clusters and particles. The key procedure for this process is the reaction between silver ions and chelating agent (EDTA) for forming a soluble silver chalate before mixing with the PZT solution, to prevent the precipitate reaction between silver ions and some organic radical. With this process, we prepared the composite thin films with silver particles of 1—10 nm in diameter in the crystallized PZT matrix[6].

Then, with similar methods, we successfully prepared $BaTiO_3$-Ag nanocomposite thin film, and studied the relationship between the microstructure and the preparation conditions (composition and condensation of the precursor solution, temperature of reacting solution, drying and heat-treatment, etc.)[10] On this basis, the investigation on the formation process of the nanocomposite was carried out and the mechanism of the process was proposed[11].

A research group led by Dr. Chakravorty, an Indian material scientist, reported the preparation and dielectric properties of PZT-Ni nanocomposite for the first time in 1995[12]. This composite was also prepared via sol-gel process. A heat-treatment process should be carried out in H_2 atmosphere to reduce Ni ions into atoms.

Yamashita et al. in the National Industrial Institute of Japan and Yao et al. in Xi'an Jiaotong University of China carried out the research on the composite of ferroelectric and metal particles. The former studied the effect of doping Ag nanophase on the ferroelectricity and other physical properties[12]; and the latter paid attention to the I-V characters of $BaTiO_3$-Ag composite[13]. The preparation method for both materials is based on ceramic method, i.e. mixing silver salt with the precursor powders of matrices. The silver ions should be reduced spontaneously. The particles in the samples prepared with this method were quite large, so it seems not suitable for the preparation of nanocomposites.

The composite of ferroelectric and atomic clusters (fullerines) is the second kind of ferroelectric-based nanocomposites. This composite was firstly prepared by a corporation run by the author and Dr. Xiao Rongfu, a professor of the Hong Kong University of Science and Technology[15]. The main preparation process includes solving C_{60} into a mixing solvent of toluene and 2-methoxyethanal, then mixing this solution with precursor solution of $BaTiO_3$, and making gel film with well-used sol-gel process. A fast annealing followed to have $BaTiO_3$ crystallized without affecting the state of C_{60}. It is indicated that most of C_{60} is in the state of molecule, not in crystal.

Recently, we have prepared a new ferroelectric-based nanocomposite with ferroelectric and II-VI semiconductor quantum dots[16]. As compared with the previous two classes of materials, the preparation of this composite is more difficult. A problem encountered is preventing the group II metal ions from inter-diffusion between the matrix and the nanophase. We solved this problem by two ways: (i) precursors of II-VI semiconductor were introduced into the pores in porous glassy matrix in the form of liquid or gas, then the composite was produced by suitable heat-treatment; (ii) preparing the colloids of II-VI semiconductors at first, then mixing it with precursor solution of ferroelectrics, and using the mixed solution as the precursor of the nanocomposite. It was indicated that the former method is suitable for the preparation of composite with the QD size of about 10—20 nm, whereas the latter is suitable for that with QD size of 1—5 nm.

3 Dielectric properties of the composites

As ferroelectrics are characterized by their special dielectric properties, researchers paid much attention to the effect of the nanophase on the dielectric properties of ferroelectric matrix. On the other hand, dielectric properties are the basis of realizing the environment of high-dielectric and high-field. So, the studies on the dielectric properties of the nanocomposites are of great importance.

For a composite composed of normal dielectric and conducting particles, considering the space charge in the conducting particles induced by electric field, the relationship between dielectric constant ε and the volume fraction of the conducting phase, P, should obey the percolation law:

$$\varepsilon \propto (P - P_c)^{-s}$$

whereas P_c is a critical value of connection between the particles, s a constant for certain material system. For ferroelectric-metal nanocomposite system, researchers reported quite different results. In their studies on PZT-Ni nanocomposites, Chakravorty[12] found that the dielectric constant increased with the introduction of Ni particles. While the volume fraction of the Ni increased from 0 to 0.06 and the particle size reached 7.6 nm, the dielectric constant of materials increased from 223 to 410, and the dielectric loss also increased, in good agreement with percolation law. Similar result was also observed by Hwang et al. in PZT-Ag system[13]. However, the results on $BaTiO_3$-Ag nanocomposite reported by Zhou[17] and on PMN-PT-Ag system by Sato[18] showed that the relationship between dielectric constant and the volume fraction of the diffusion phase were against the percolation law.

Zhou found that in $BaTiO_3$-Ag nanocomposite the dielectric constant slightly declined and dielectric loss increased with the increase of Ag volume fraction below the Curie point of $BaTiO_3$. The phenomenon that both dielectric constant and dielectric loss decrease with the increase of Ag fraction, which obeys the percolation law, can only be observed above Curie temperature. This result indicates that the contribution of the metal particles to the dielectric constant of the composite is not just a simple accumulation, an interaction between the metal particles and the ferroelectric domain may alter the dielectric behavior of the dielectrics. Only when ferroelectric state changes into paraelectric state above the Curie temperature does the composite show the normal behavior like the other composite of dielectric and metal particles. The research result on the dielectric constant of PMN-PT-BT composite obtained by Sato showed a dramatic decrease from 21000 to 14000 in dielectric constant when the fraction of Ag is lower than 0.2%, then increased again with the increase of Ag fraction[18]. The latter was attributed to the effect of large amount of Ag on the order-disorder structure in ferroelectric relaxor matrix.

A primary study on the dielectric constant of $BaTiO_3$-C_{60} composite has also been carried out by Zhou[15]. A slight increase in dielectric constant and loss with the introduction of C_{60} was observed.

Generally, from the latest research result, the doping of the nanophase can not fundamentally change the dielectric properties of the matrix, but relatively high dielectric constant in the ferroelectric can be obtained while nanophase are doped. This ensures the feasibility for the construction of nano-meso system modified by high-dielectric and high-field.

4 Optical properties and environmental effect of high-dielectric and high-field

Ferroelectric-based nanocomposite is a very new functional material. The studies on the optical properties of this material are still seldom. The related studies are mainly carried out by the author's group[19]. Even just at the starting in this area, some experiment phenomena are still quite exciting. These phenomena not only reflect the novel properties of the high-dielectric and high-field modified nano-meso system, but also show a promising prospect of ferroelectric-based nanocomposite in the application of nonlinear optics and electroluminescence.

Figure 1 shows the absorption spectra of $BaTiO_3$-Ag nanocomposite thin films with different annealing temperatures. The main absorption peak was due to the coherent resonance absorption of surface plasma in the metal particles. With the increase of annealing temperature, the absorption peak shifted to long-wavelength drastically. An important factor causing this red-shift is the modification of dielectric constant of the matrix on the coherent frequency of the surface plasma of metal particles. According to Mie theory[20], the frequency can be described as

$$\omega_r = \omega\left(\frac{\varepsilon_d}{2\varepsilon_m + \varepsilon_d}\right)^{1/2},$$

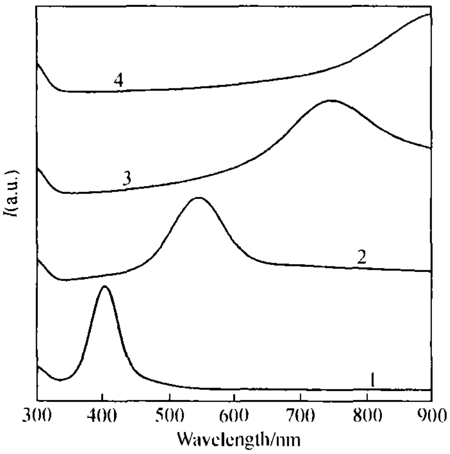

Fig. 1. Absorption spectra of $BaTiO_3$-Ag nanocomposite thin films treated at 300℃ (curve 1), 400℃ (curve 2), 500℃ (curve 3) and 600℃ (curve 4).

where ω_r is the frequency of coherent resonance of the surface plasma of the metal particles in composite, ω the frequency for bulk metal, ε_d the dielectric constant of the diffusing phase, and ε_m the dielectric constant of the matrix. With the increase of annealing temperature, the degree of crystallization for the matrix increases, so the dielectric constant of the matrix increases. This will cause a decrease in the frequency of absorption peak of the metal particles, from blue to infrared region. This is a typical example of the modification rule of high-dielectric matrix on the optical properties of the nanophase in ferroelectric-based nanocomposite.

Another more interesting phenomenon is the enhancement of the second order optical nonlinearity of ferroelectric thin film by doping metal nanoparticles. We determined the index of second order optical nonlinearity of the polarized $BaTiO_3$-Ag nanocomposite by measuring the intensity of second-order harmonic generation (SHG) pumped by a YAG laser. An obvious enhancement of the SHG took place due to the doping of Ag into $BaTiO_3$ thin film. The $\chi^{(2)}$ in the sample with molar ratio Ag/Ba = 0.01 is twice as high as that in pure $BaTiO_3$ thin film. The mechanism for this phenomenon is not very clear, but it ought to be related to the behavior of the nanoparticles in the high polarization field. As ferroelectric thin films are excellent second-order nonlinear optical materials, and the doping of Ag particles can lead to an increase of its nonlinearity, we can predict that the ferroelectric-metal nanocomposite should be a very promising candidate for the next generation material for nonlinear optical application[21].

Recently we studied the optical properties of $BaTiO_3$-CdS, a nanocomposite of ferroelectric and semiconductor quantum dots[21]. An intense photoluminescence was observed while the sample was excited by ultraviolet ray. Its typical spectra are shown in fig. 2, which include two groups of emission bands. One of them formed by a narrow main peak at 465 nm and some satellite peaks, which can be attributed to the band-edge transition of CdS, while the blue-shift and the satellite band should be the typical character of QDs. The other is a broad band covering 550—650 nm, which can be assigned to the surface state of the QDs. Similar to other QD composite, the wavelength and intensity is related with the condition of material preparation. Even though there is no essential difference in photoluminescence between this material and other QD materials.

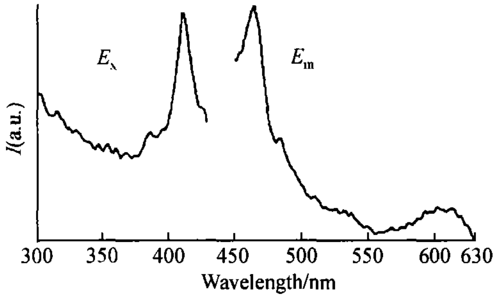

Fig. 2. Photoluminescence emission and excitation spectra of CdS QD's in $BaTiO_3$ matrix.

5 Application example: a new concept for electroluminescence

As shown above, we can predict that ferroelectric-based manocomposite possesses many potential functions of great application value. Even the research work done is still very primary and incomplete, some prospects are appearing gradually with the progress in of the research, an example is the enhancement of the second order optical nonlinearity. These materials also show a promise in electrooptical modulation, pyroelectric and piezoelectric material and others. Here we would like to put forward a new concept to realize a novel electroluminescence with very low driving voltage using the ferroelectric-QD nanocomposite.

High-field electroluminescence is a luminescence process in semiconductor excited by the collision ionization and tunneling of overhot electron induced by high alternate electric field. Alternate current electroluminescence (ACEL), which is commonly used in flat panel display, belongs to this mechanism. Because a high-field intensity is needed for excitation, the driving voltage of these devices was often higher than hundreds or even thousands of volts. Many efforts on lowering the driven voltage have been made over the past three decades, however, almost no eventual breakthrough occurred.

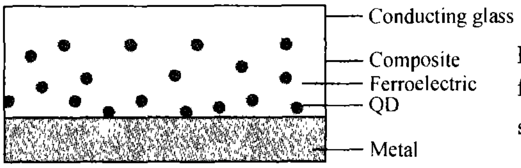

Fig. 3. Schematic diagram of low driving-voltage ACEL based on the nanocomposite of ferroelectric and semiconductor QDs.

Meanwhile putting forward the concept of meso-physical system modified by high dielectric and high field, we designed a new EL with the structure as shown in figure 3.

The EL have a very simple sandwich structure, the middle layer is the composite thin film of ferroelectric and II-VI QD's with EL property, a metal electrode and a transparent glass electrode are on both sides separately. In this structure, if the dielectric constant of the ferroelectric is high enough, even when a very low external voltage is applied between two electrodes, a sufficiently high local field can be induced, which can excite EL in QDs. Theoretical estimation shows that the driving voltage of this device should be very low. If this tentative idea is realized, the dream for many years about the integration of light emission devices with silicon-based IC should come true.

Finally, we would like to point out that, as ferroelectric-QD composites provide an effective mechanism for the excitation of QDs with external field, it is possible to realize population inversion of QDs. So, if the semiconductor crystallites in ferroelectric matrix possess a resonantor structure, a new type of QD laser can be made.

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