Capacitance-conductance investigation on the phase transitions in Ga nanoparticles

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Abstract

We have reported on coupled capacitance-conductance measurements on Ga nanoparticles embedded in vitreous matrices. The melting of nanoparticles was clearly detected as an abrupt increase in the capacitance vs. temperature scans. The influence of the embedding matrix and of the frequency of the applied field on the dielectric response was checked. The presence of a hysteresis cycle between melting and solidification has been detected. The technique allows the identification of the various solid phases of confined Ga.

Keywords

Gallium nanoparticles; Capacitance-conductance; Phase transitions

1. Introduction

It is well known that the thermodynamic properties of metal nanoparticles present strong deviations with respect to the bulk ones. One of the most significant examples is given by the melting temperature, which is lower in the nanoparticles and exhibits a strong size dependence [1] and [2].

Bulk α gallium is a metallic molecular crystal; it has a covalent nature and is sometimes considered as a semimetal [3]. The melting temperature of the α phase is low: $T_m(\alpha)\sim302.7$ K. The α phase is stable, but other metastable metallic phases (labeled as β, γ, δ, ε) exist, each one characterized by different structural parameters and, consequently, different melting points, lower than $T_m(\alpha)$.

When Ga is dispersed inside a matrix, the α phase is not found, since its density is lower than the liquid one [4] and [5], but some of the metastable phases appear and are now stable. Until now, few investigations that use X-ray diffraction and calorimetric techniques have been performed on macroscopic Ga systems in a matrix [4] and [5]. The case of the nanometric particles still remains to be explored. The experimental situation is rather complicated due to the fact that: (i) a mixture of the different phases is expected; and (ii) melting of the various phases is shifted to lower values due to the size effect [1] and [2].

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In this paper, the capacitance and conductance variations as a function of temperature have been measured to identify phase transitions in Ga nanoparticles embedded in different dielectric matrices. The simultaneous measurement of these two quantities allows the knowledge of both the real and imaginary part of the dielectric function.

2. Experimental

The samples investigated were grown by an evaporation-condensation self-organized process in ultra high vacuum [6]. Ga nanoparticles were embedded in amorphous matrices (either SiO_x or MgF_2) on sapphire substrates. In order to improve the signal-to-noise ratio, several layers of nanoparticles were grown. Samples with different nanoparticle radii and with the same total amount of Ga were prepared and investigated. Reference samples, without nanoparticles, were also grown.

The bottom electrode has been a silver layer evaporated between the substrate and the matrix+Ga system (see Fig. 1). The second electrode was a pin kept in contact with the opposite side of the sample by a spring system. The accuracy of the experimental data measured using such kind of electrodes has been evaluated to be approximately 10%.

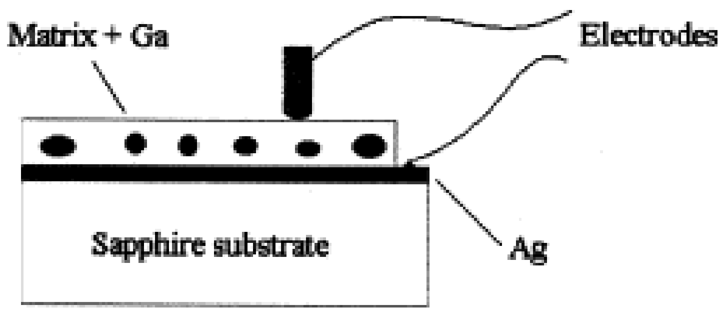

Fig. 1. - Sketch of the experimental set-up.

Capacitance and conductance measurements were performed by a general radio 1616-A capacitance bridge at different frequencies (~1 KHz and ~50 KHz). For low temperature measurements, a He-closed circuit cryostat was employed. The rate of the temperature variation was kept between 1 and 2 K/min.

3. Capacitance and conductance measurements

In Fig. 2, the capacitance and conductance of the sample Ga5MgF_2, containing Ga nanoparticles with a 10-nm average radius, embedded in a vitreous MgF_2 matrix, are reported as a function of the increasing temperature.

Thin Solid Films Volume 380, Issues 1–2, 22 December 2000, Pages 230–232 doi:10.1016/S0040-6090(00)01529-7

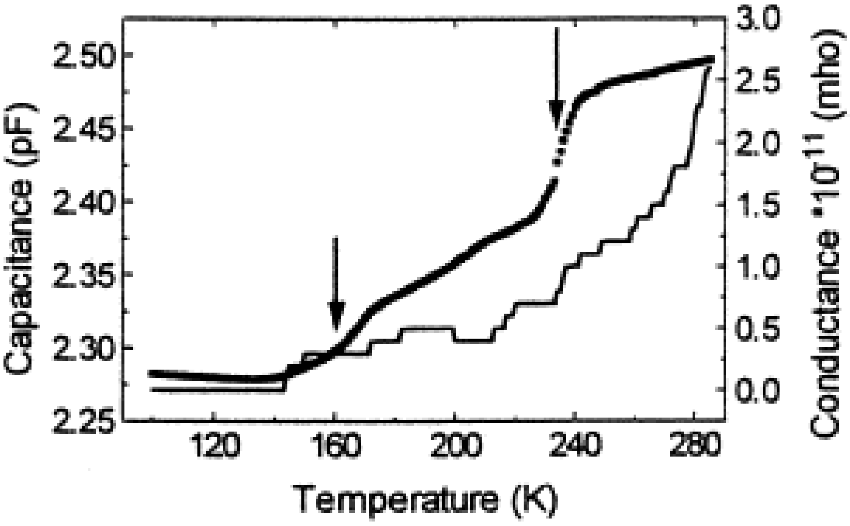

Fig. 2. - Capacitance (solid squares) and conductance (continuous line) of the sample $Ga5MgF_2$ by increasing the temperature.

The conductance exhibited a roughly exponential increase with temperature, typical of glassy materials [7]; as expected, the matrix contribution was dominant, since its resistivity is by far larger than the resistivity of the metal nanoparticles.

The capacitance exhibits two main structures, marked by arrows. The first one, between 150 and 175 K, was also detected for the reference sample (not reported here), and could be attributed to a dielectric relaxation of the matrix. It should be accompanied by a structure also in the conductance, but when the signal is below 10^{-11} mho, a careful identification of possible structures is very difficult.

The abrupt increase in the capacitance between 225 and 240 K was not observed in the reference sample (see Fig. 3). From the results of previous investigation on bulk Ga and on nanoparticles of different metals [1], [2], [3], [4] and [5], we expect the melting of the nanoparticles to occur in this temperature range. This fact suggests that the strong increase in capacitance (~3.5% in few K) is due to a solid-to-liquid transition, as also supported by the lineshape analysis [8]. Moreover, we point out that the temperature range where this structure takes place is frequency independent, supporting the interpretation of the occurrence of a real phase transition rather than a dielectric relaxation.

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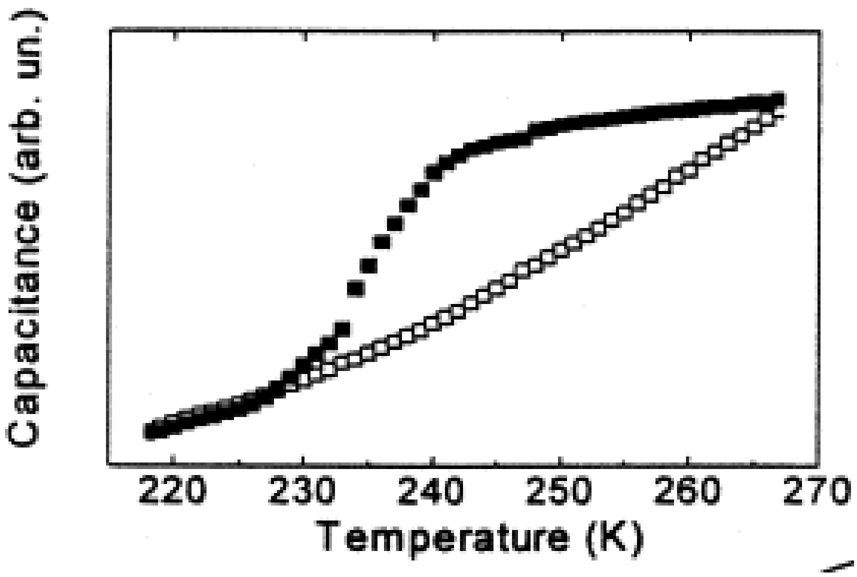

Fig. 3. - Comparison between the capacitance behaviors of the sample Ga5MgF_2 (solid squares) and of the reference sample (open squares) by increasing the temperature.

A similar behavior has also been observed in the capacitance plots of the sample Ga2SiO_x, containing Ga nanoparticles with a 4-nm average radius embedded in an SiO_x matrix (see Fig. 4). Here, we report the data from both increasing and reducing the temperature. As expected, the structure attributed to the liquid–solid transition was detected at a temperature lower than the melting one. The phenomenon has been well investigated in the past decade [1] and [2].

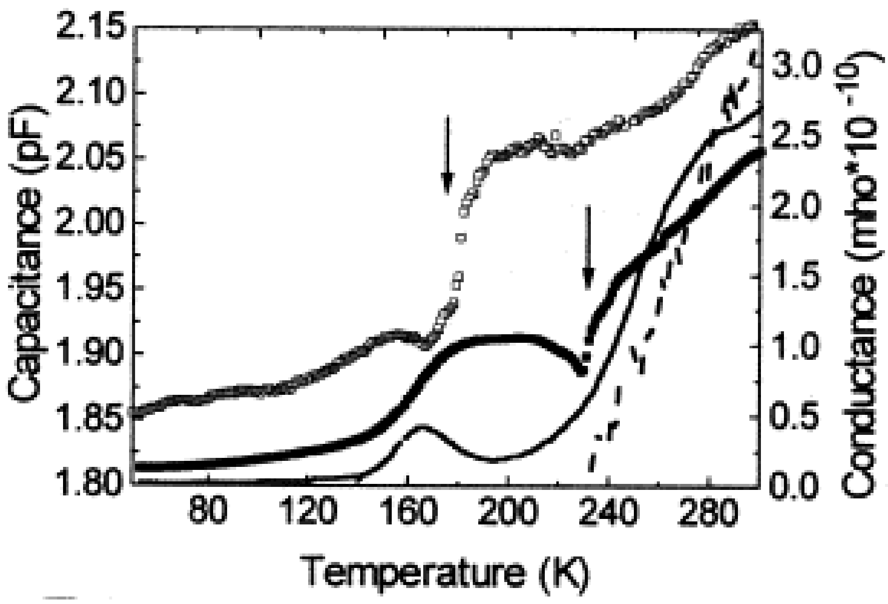

Fig. 4. - Capacitance of the sample Ga2SiO_x increasing (solid squares) and reducing (open squares) the temperature; the conductance is reported too, both increasing (continuous line) and reducing (dashed line) the temperature. The phase transition is marked by an arrow.

Thin Solid Films Volume 380, Issues 1–2, 22 December 2000, Pages 230–232 doi:10.1016/S0040-6090(00)01529-7

The decrease in capacitance immediately before melting is an indication of the progressive disordering of the system [8]. A feature to observe in this plot is the strong evidence of matrix dielectric relaxation in the measurement performed by increasing the temperature (sigmoidal shaped structure in the real part of the dielectric function and peak-shaped structure in the imaginary part) at approximately 160 K.

In conclusion, the study of the capacitance and conductance of metal nanoparticles, embedded in an amorphous matrix as a function of temperature, allowed us to identify the melting point of the nanoparticles. Due to its high sensitivity, this technique also appears very promising for the identification of the different solid phases of Ga on the basis of their melting temperature. In fact, by optimizing the electrode system, we were able to detect, in selected samples, detailed features, at temperatures corresponding to the melting of different Ga phases.

A new, more suitable electrode disposition is being developed, with the aim of: (i) optimizing the signal and detect secondary structures; (ii) obtaining a quantitative evaluation of the real and imaginary part of the dielectric functions.

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Thin Solid Films Volume 380, Issues 1–2, 22 December 2000, Pages 230–232 doi:10.1016/S0040-6090(00)01529-7