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Dielectric properties of GaN nanoparticles

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Three kinds of GaN samples (hexagonal coarse-grain powders, hexagonal nanoparticles and cubic nanoparticles) were synthesized by different methods. The room-temperature frequency spectra of the relative dielectric constant and that of the dielectric loss were measured in the frequency range of 100 Hz to 10 MHz. Analysis of these spectra indicates that the grain size of samples has great influence on the dielectric behavior of samples whereas the crystallography symmetry almost has no impact on the relative dielectric constant. © *2001 Kluwer Academic Publishers*

1. Introduction

The synthesis and characterization of nanoparticles are currently an area of intense theoretical and experimental research. The revelation that physical properties of nanoparticles are bound to be appreciably different from corresponding materials excited much interest in the study of nanoparticles [1, 2]. In particular, the synthesis of GaN nanoparticles has gained great efforts due to their potential uses in both mesoscopic research and future development of nanodevices [3–5]. As a wide direct band gap semiconductor, GaN is a promising material for fabrication of blue light emitting diodes (LEDs) and laser diodes (LDs) [6]. It has been theoretically predicted that the realization of LEDs and LDs with GaN nanoparticles in the active layer would lead to improved optical characteristics, such as low threshold current and weak temperature dependence of the threshold current [7]. In addition, the quantum-confinement effect of GaN nanoparticles can bring enhanced nonlinear optical properties and emission characteristics. Up to now, the physical properties of GaN nanoparticles have been widely investigated. However, experimental studies on the dielectric properties of GaN nanoparticles are limited. In this paper, we report the dielectric behavior of both hexagonal and cubic GaN nanoparticles under the measuring frequency of 100 Hz to 10 MHz. In particular, the effects of the grain size of samples are discussed.

2. Experimental procedures

The nanoparticles of cubic GaN were synthesized by the ammonothermal method. The procedure was as follows: appropriate amount of Ga metal (99.999% purity) and NH_4I (99.9% purity) were weighed according to the molar ratio of 1:1. Then the raw materials were put into a platinum-linear stainless-steal autoclave of 30 ml capacity, and then the autoclave was filled with liquid ammonia up to about 70% of the total volume. The autoclave was maintained at 300°C for 48 h. The inner pressure is estimated to be above 2000 atm. After reaction, the autoclave was allowed to cool naturally to room temperature. The final products were collected and washed with ethanol and distilled water. Then they were dried and the nanoparticles of cubic GaN were obtained.

By the same method as mentioned above, hexagonal GaN nanoparticles can be prepared [5]. But for this time, the mineralizer is NH_4Cl (99.9% purity), and the molar ratio of Ga to NH_4Cl is 82:18. In addition, the autoclave was maintained at 350–500°C for 72–120 h.

As to the preparation of the coarse-grain powders of hexagonal GaN, a gas reaction route was used [8]. In a typical run, proper amount of Ga metal (99.999% purity) was loaded into a pure-quartz reaction boat which was placed in a horizontal tube furnace and heated under an Ar flow rate of about 200 ml/min up to 1000°C. Then Ar gas was stopped and NH_3 gas (99.9% purity) was transferred at a flow rate of about 200 ml/min for 4–6 h. Under these conditions, pure hexagonal GaN coarse-grain powders can be obtained.

In our experiments, three samples with different grain size were used. For the purpose of reference, they are listed in Table I. The X-ray powder diffraction (XRD) patterns of these samples were recorded on a Philips MPD diffractometer with Cu K_α radiation (Fig. 1). The analysis of Fig. 1 indicates that the samples are pure hexagonal GaN coarse-grain powders, pure hexagonal GaN nanopaticles and pure cubic GaN nanoparticles, respectively. Using these XRD patterns and the Scherrer formula, the grain size of samples can be determined (Table I).

Disk-shape samples with 12.6 mm in diameter and 1.24 mm in thickness were prepared by compacting the powders under a uniaxial pressure of 29.4 MPa. Both the faces of samples were coated with a layer of silver conducting paint. The values of the sample capacitance (C) and the dielectric loss ($\tan\delta$) at different frequencies (f) (100–10 MHz) were then determined

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TABLE I Samples with different grain size

Sample	Crystallographic system	Preparation method	Grain size
GaN-1	Hexagonal	Gas reaction	1 μm
GaN-2	Hexagonal	Ammonothermal	20 nm
GaN-3	Cubic	Ammonothermal	32 nm

on HP-4274A and 4275A LCR meters with a signal voltage of 0.5 V_{rms}. The values of C and $\tan\delta$ of the sample were recorded by a computer. Using the following equation, the relative dielectric constant (ε_r) can be easily calculated:

$$\varepsilon_r = \frac{d}{\varepsilon_0 A} C \qquad (1)$$

where ε_0 is the dielectric constant in vacuum, d and A are the thickness and the area of the sample, and C is the measured value of sample capacitance. Then dielectric spectra of the sample can be drawn by using the data of ε_r, $\tan\delta$ and f.

3. Results and discussion

Fig. 2 shows the room-temperature frequency spectra of ε_r of GaN samples. It can be seen that the frequency dependence of ε_r of these samples tends to follow a general pattern. With the increase of f from 100 Hz to 10 MHz, ε_r decreases monotonously. In the low frequency range (from 100 Hz to 1 kHz), ε_r reduces rapidly with the increasing f. When $f = 1$ kHz, ε_r decreases much slowly and remains almost unchanged after f rises to 100 kHz.

However, comparison of ε_r of GaN-1 with that of GaN-2 indicates that when f is in the range of 100 to 400 Hz, ε_r of GaN-2 is much larger than that of GaN-1. Table II gives the values of ε_r of samples at different frequencies. For GaN-1, ε_r is 74.31 at 100 Hz, but for GaN-2, ε_r is 176.65 at 100 Hz and more than twice as much as that of GaN-1. These results show that GaN nanoparticles have much higher ε_r in comparison with GaN coarse-grain powders. According to Zhang [9], nanostructured materials have about 10^{19} interfaces per cm^3, much more than those of bulk solids. In our experiments, GaN nanoparticles were compacted under high pressure (29.4 MPa), so interfaces with a large volume fraction in the nanostructured sample must contain a large number of defects, such as dangling bonds, vacancies, vacancy clusters and microporosities, which can cause a change of positive and negative space charge distributions in interfaces. Exposed to an external electric field, positive and negative space charges in interfaces. Exposed to an external electric field, positive and negative space charges in interfaces move towards negative and positive poles of the electric field, respectively. When they are trapped by defects, a lot of dipole moments will be generated. Consequently, space-charge polarization occurs in interfaces of GaN nanoparticles. Because the volume fraction of these interfaces is very large, space-charge polarization plays an important role in the contribution to ε_r of GaN nanoparticles. But for GaN coarse-grain powders, the volume fraction of interfaces is very small, so space-charge polarization in coarse-grain powders is too weak to be observed. Therefore, due to the existence of space-charge polarization, ε_r of GaN nanoparticles is higher than that of coarse-grain powders.

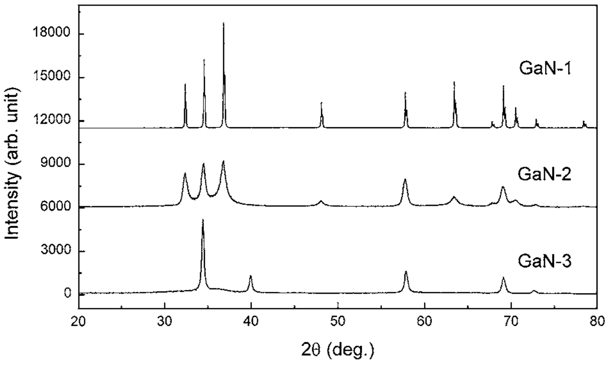

Figure 1 X-ray powder diffraction pattern of GaN samples with Cu K_α radiation.

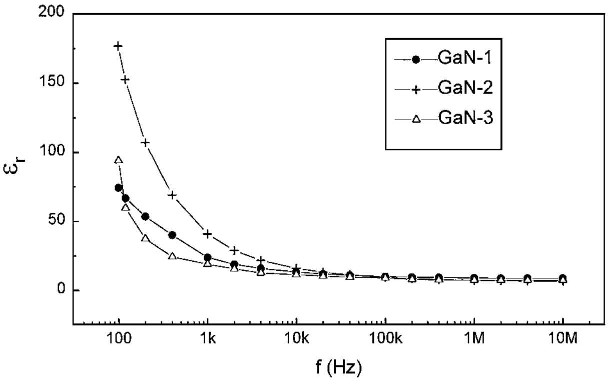

Figure 2 Room-temperature frequency spectrum of the relative dielectric constant of GaN samples.

In addition, acting as shollow donors, a great quantity of nitrogen vacancies exists in GaN [10, 11]. Hence interfaces of GaN nanoparticles possess a lot of nitrogen vacancies. A positive nitrogen vacancy together with a negative nitrogen ion gives a dipole moment. Thus, lots of dipole moments will be formed. Under the action of an external electric field, these dipole moments will rotate. Consequently, rotation direction polarization takes place in interfaces of GaN nanoparticles. However, for GaN coarse-grain powders, due to the lack of interfaces and high density, this kind of polarization can hardly appear. Therefore, rotation direction polarization is another reason for GaN nanoparticles have higher ε_r than that of coarse-grain powders.

From Table II, it is clear that in the low frequency range (100–1 kHz), ε_r of GaN-2 is larger than that of

TABLE II The values of ε_r of samples at different frequencies

	f				
Sample	100 Hz	200 Hz	400 Hz	1 KHz	10 MHz
GaN-1	74.31	53.37	39.95	28.73	8.67
GaN-2	176.65	106.92	68.99	40.68	6.49
GaN-3	93.93	37.20	24.16	31.04	6.22

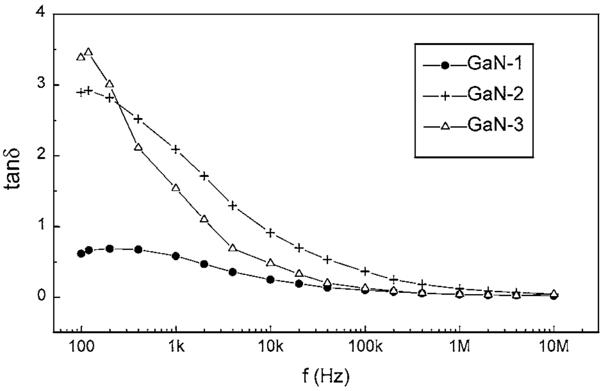

Figure 3 Room-temperature frequency spectrum of the dielectric loss of GaN samples.

GaN-3. As shown in Table I, the grain size of GaN-2 and GaN-3 is 20 nm and 32 nm, respectively. Therefore, that GaN-2 has larger ε_r than that of GaN-3 is mainly due to the size effect of ε_r [12]. From Fig. 2, it can be seen that when f rises to 100 kHz, ε_r of GaN-2 is close to that of GaN-3. According to Table II, ε_r of GaN-2 at 10 MHz is 6.49 while that of GaN-3 is 6.22. As Wang *et al.* reported [13], under optical frequency, ε_r of cubic GaN is 5.16 while that of hexagonal GaN is 5.62 in the (001) direction and 5.40 in the perpendicular direction.

Fig. 3 gives the room-temperature frequency spectra of the dielectric loss ($\tan\delta$) of GaN samples. It can be seen that the common feature of these spectra is that a small peak appears in each spectrum. This is related to electric relaxation polarization [14]. Comparison between GaN-1 and GaN-2 indicates that at low f, $\tan\delta$ of GaN-1 is much lower than that of GaN-2. As mentioned above, due to the interfaces with a large volume fraction, two kinds of polarization (space-charge polarization and rotation direction polarization) take place in GaN-2; however, for GaN-1, because the number of interfaces is very small, both kinds of polarization do not occur. According to the theory of the dielectric polarization, space-charge polarization and rotation direction polarization appear in the low frequency range and will cause energy loss, so $\tan\delta$ of GaN-2 is much higher that of GaN-1. Since both GaN-2 and GaN-3 are nanoparticles and have the same kinds of polarization, $\tan\delta$ of both samples is similar.

4. Conclusion

The grain size of samples has a great influence on the dielectric behavior of GaN materials. Due to the existence of interfaces with a large volume fraction, hexagonal GaN nanoparticles have much higher ε_r than that of hexagonal GaN coarse-grain powders. At high frequency ($f = 1$ MHz), ε_r of hexagonal GaN nanoparticles is a little higher than that of cubic GaN nanoparticles.

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References

1. R. W. SIEGEL, H. HAHN, S. RAMASAMY, *et al.*, *J. Phys.* **49**(C5) (1988) 681.
2. T. HALICIOGLU and C. W. BAUSCHLICHER, *Rep. Prog. Phys.* **51** (1988) 883.
3. Y. XIE, Y. T. QIAN, W. Z. WANG, S. Y. ZHANG and Y. H. ZHANG, *Science* **272** (1996) 1926.
4. A. C. FRANK, F. STOWASSER, H. SUSSEK, H. PRIZTKOW, C. R. MISKYS, O. AMBACHER, M. GIERSIG and R. A. FISHER, *J. Am. Chem. Soc.* **120** (1998) 3512.
5. X. L. CHEN, Y. G. CAO, Y. C. LAN, X. P. XU, J. Q. LI, K. Q. LU, P. Z. JIANG, T. XU, Z. G. BAI, Y. D. YU and J. K. LIANG, *J. Cryst. Growth* **209** (2000) 208.
6. S. NAKAMURA, *Science* **281** (1998) 956.
7. Y. ARAKAWA and H. SAKAKI, *Appl. Phys. Lett.* **40** (1982) 939.
8. X. L. CHEN, Y. C. LAN, J. K. LIANG, X. R. CHENG, Y. P. XU, T. XU, P. Z. JIANG and K. Q. LU, *Chin. Phys. Lett.* **16** (1999) 107.
9. BIN CHEN, JIAN SHA, XISHENG YE, ZHENGKUAN JIAO and LIDE ZHANG, *Science in China* **42** (1999) 510.
10. P. BOGUSLAWSKI, E. L. BRIGGS and J. BERNHOLC, *Phys. Rev. B* **51** (1995) 17255.
11. P. PERLIN, T. SUSKI and H. TEISSEYRE, *Phys. Rev. Lett.* **75** (1995) 296.
12. C. M. MO, L. D. ZHANG and G. Z. WANG, *Nanostructured Materials* **6** (1995) 826.
13. R. WANG, *J. Phys. Chem. Solids* **58** (1997) 913.
14. Z. D. GUAN, Z. T. ZHANG and J. S. JIAO, "Physical Properties of Inorganic Materials" (in Chinese) (Tsinghua University Press, Beijing, 1992) p. 327.

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