

Piezoelectric Properties of BaTiO₃ Nanoparticles with Surfaces Modified by Hydroxyl GroupsN. Emelianov¹, P. Belov¹, A. Sizov², O. Yacovlev²¹ Kursk State University, 33, Radishcheva Str., Kursk, Russia² South-West State University, 94, 50 Let Octyabrya Str., Kursk, Russia

(Received 19 May 2014; published online 15 July 2014)

Piezoelectric properties of nanoparticles BaTiO₃ with spherical shape, diameter of 20-200 nm, the surface-modified hydroxyl (-OH) groups studied by piezoelectric force microscopy. Measured value of piezoelectric coefficient $d^*_{33} = 27$ pm/V, which is close to the value obtained for the 100 nm particles BaTiO₃.

Keywords: Nanoparticles BaTiO₃, Surface modification, Piezoelectric force microscopy.

PACS numbers: 61.46, 77.84, 77.65.Bn

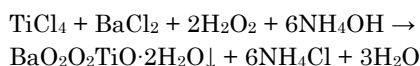
1. INTRODUCTION

Composite materials based on BaTiO₃ nanoparticles in polymer matrices are promising for manufacturing components of micro- and nanoelectronics. The most important characteristic of the composite material is its uniformity of electrophysical properties. However, nanoparticles of barium titanate obtained by the majority of known methods cannot be uniformly dispersing in the polymer matrix. One way to overcome this problem is to modify the surface of the nanoparticles, for example, hydroxyl (-OH) groups [1].

In addition, quantum chemical calculations show that the modification of the structure particles of these groups can significantly affect the magnitude and kinetics of their polarization.

2. EXPERIMENTAL SECTION

Barium titanate nanoparticles were synthesizing by the peroxide method. Precursor was synthesizing according to reaction:



The resulting precipitate was filtered off, washed out and dried. Heat treatment was performing in air during one hour at a temperature of 700 °C. By scanning electron microscopy revealed that the synthesized BaTiO₃ nanoparticles have a spherical shape with a diameter of 50-200 nm. Splitting reflex (200/002), according to X-ray analysis (GBC EMMA, CuK α), indicates the presence of the tetragonal phase, which is also confirmed by the presence of the peak 304 cm⁻¹ in the Raman spectrum of light. Analysis of the FT-IR spectrum (FSM 1201, Monitoring) shows the presence the band at 578 cm⁻¹ represents the Ti-O vibration of BaTiO₃. Broad peak near 3400 cm⁻¹ is assigned to the stretching mode of surface -OH. The peaks at around 1300-1700cm⁻¹ belong to the bending mode of H-O-H (Fig. 1).

The piezoelectric response BaTiO₃ nanoparticle was investigating using by the method of piezoelectric force microscopy (Solver Next, NT-MDT, cantilever CSG-01, resonant frequency 25.12 kHz) in a known manner. The particles are dispersed have been in aqueous etha-

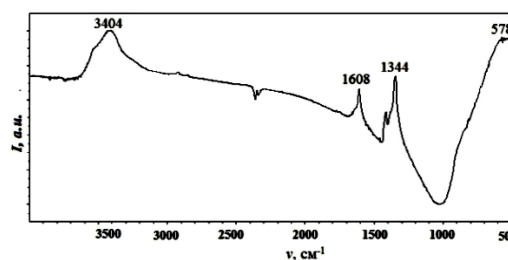


Fig. 1 – FT-IR spectrum nanoparticles BaTiO₃ obtained peroxide way

nol (96 %) and deposited on the lower electrode, which is a layer of gold (thickness 40 nm) was deposited on a silicon substrate [111] by magnetron sputtering. During scanning the surface of nanoparticles on the cantilever applied AC voltage 3 V with a frequency equal to the resonant frequency of the cantilever. Image of the surface topography and amplitude piezoelectric response single nanoparticles is shown in Fig. 2.

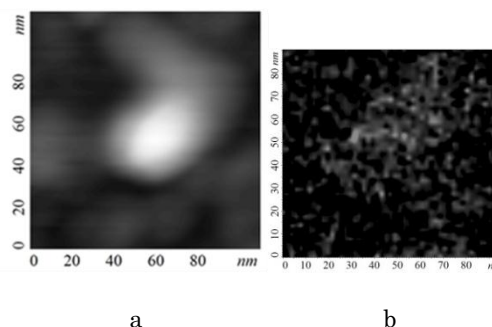


Fig. 2 – Simultaneously obtained topographic (a) and amplitude PFM (b) images nanoparticle BaTiO₃

Standard PFM hysteresis (amplitude x phase versus bias voltage, Fig. 3a and butterfly-shape curves (amplitude versus bias voltage, Fig. 3b for BaTiO₃ nanoparticles are shown in Fig. 3. To convert the value of the signal DFL, reflecting the amplitude of the cantilever deflection in nanometers, calibrates on power curve DFL (Height).

Multiplying the slope of the curve DFL (Height) by the amount of the DFL signal was obtained value of the maximum displacement of 0.21 nm at a bias voltage of

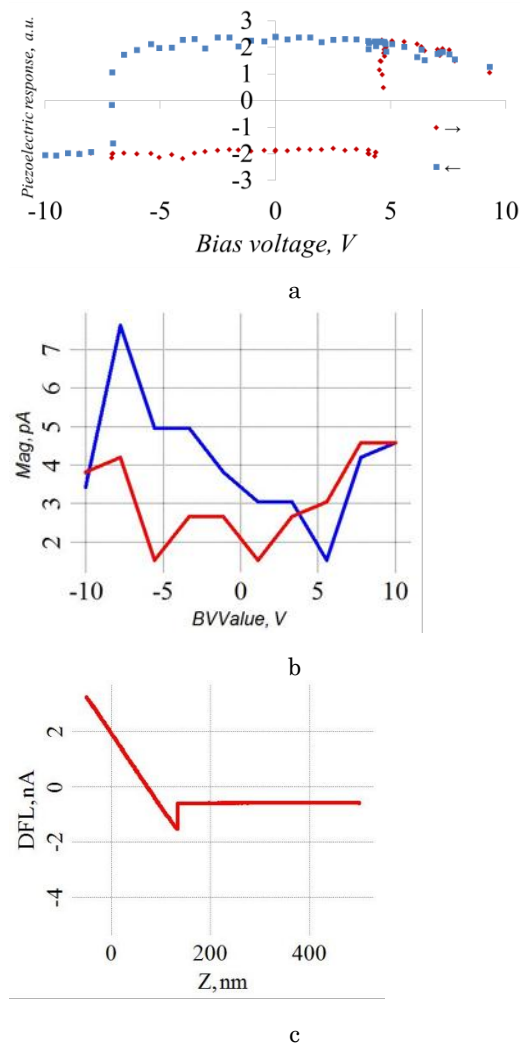


Fig. 3 – a) Standard PFM hysteresis curve (amplitude \times phase versus bias voltage), b) butterfly-shape curve (amplitude versus bias voltage) for nanoparticle BaTiO₃ and c) power curve DFL (Height)

– 7.9 V. We have calculated the values of piezoelectric coefficients, d_{33} , which are near 27 pm/V ($A = QV_{ac}d_{33}$, where A is piezo-amplitude, Q is the quality factor

REFERENCES

1. Chia-Chen Li, Shinn-Jen Chang, Jyh-Tsung Lee, Wei-Sheng Liao, *Colloid. Surface A* **361**, 143 (2010).
2. Zhao Deng, Ying Dai, Wen Chen, Xinmei Pei, Jihong Liao, *Nanoscale Res. Lett.* **5**, 1217 (2010).
3. Arvids Stashansy, Johnny Chimborazo, *Philosoph. Magazine B* **82** No 10, 1146 (2002).
4. F. Peter, K. Szot, R. Waser, et al., *Appl. Phys. Lett.* **85**, 2896 (2004).

which accounts for the amplitude enhancement at tip-bias resonance and V_{ac} is the voltage), which is near to the value obtained in [2] to 100 nm cup-shaped particles of BaTiO₃.

3. RESULTS AND DISCUSSION

The polarization switching and the hysteresis loops shown in Fig. 3, demonstrate the ferroelectric nature of the obtained nanoparticles. Resulting hysteresis loops show nanoparticles polarization switching at room temperature. However, the observation of ferroelectric behavior in these BaTiO₃ nanoparticles is not without controversy. One of the possibilities is that the applied field resulted in the depletion of or accumulation of charge underneath the tip without actual ferroelectric switching. This may contribute to the hydroxyl groups on the surface of the nanoparticles. The reason for the asymmetry of the hysteresis loop can also be a polarization of surface OH-groups.

Note ambiguity influence on the polarization of the hydroxyl groups of the nanoparticles BaTiO₃ according to reports. Thus, according [3], hydrogen impurity increases the bulk ferroelectric polarization. However, the weakening of the bonds Ti-O outside of the impurity atoms leads to loss of oxygen, particularly at interfaces, and as a consequence, to reduction in the switching charge of the ferroelectrics. In [4] shows a significant increase in the piezoelectric response signal during the annealing of the hydroxyl groups on the surface of the ferroelectric film.

It should also be noted that in this setup bias voltage maximum value was ± 10 V, which could be sufficient to achieve the saturation polarization of the nanoparticles. To increase the bias an external voltage supply would be necessary.

4. CONCLUSIONS

Thus, the method set force microscopy piezoelectric response of polarization switching in the nanoparticles modified with hydroxyl groups. The magnitude of the piezoelectric coefficient d_{33} was about 27 pm/V. Influence of surface groups on the piezoelectric properties of nanoparticles requires further study.