PHYSICAL REVIEW B VOLUME 49, NUMBER 8 15 FEBRUARY 1994-II

Photoacoustic investigation of the quantum size effect and thermal properties in ZrO_2 nanoclusters

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(Received 4 October 1993)

Nanometer size ZrO_2 clusters are generated using the hydrothermal method. The physical properties of nanoclusters of ZrO_2 of different sizes have been studied by using the photoacoustic spectrum (PAS). The results show the blueshift of the cutoff wavelength of the PAS absorption edge and the absorption peak of the first-order differential spectrum. When the average grain size of the ZrO_2 nanoclusters is less than 5 nm, the blueshift of the absorption peak is 9.8 nm with respect to that corresponding to an average grain size of 90 nm. At the same time, we have observed the fine structures of the absorption edge when decreasing the average size of the nanoclusters of ZrO_2. Moreover, we have found that the thermal constant of the nanoclusters increases significantly when their average grain size is decreased. The above phenomena are related to the quantum size effect, the super surface effect, and the interaction of nanoclusters.

I. INTRODUCTION

Nanomaterials have an average grain size ranging from 1 to 100 nm, which is between the macroscopic and the microscopic range. They have peculiar structures[1-3] and many unusual properties.[4-9] In particular, when the average grain size of the nanomaterials is smaller than or equal to the quantum size[10-12] (or the de Broglie's wavelength of the electron), the energy states which are originally in the continuous conduction band and the valence band will be split or shifted. At the same time, since there are a lot of atoms and molecules of ZrO_2 nanoclusters in the surface state or near the surface state, there are a lot of interfaces between the nanoclusters and the medium, or close to the nanoclusters. As the atoms in the interface are very active, they interact with the nearby media very easily. Apparently, these interfaces will affect the physical properties of the nanoclusters or the nanocrystals. The nanoclusters are the basic units which construct the nanomaterials, so it is very important to study the physical properties of the nanoclusters themselves.

We note that the samples for getting UV or IR absorption spectra should be transparent. In order to obtain a thin piece of transparent sample or a solution, additives should be added such as KBr, NaCl, or other solvents. However, in our case, this will change the original surface states of the nanoclusters. In the photoacoustic spectrum (PAS), the addition of additives is not required. We can directly measure and compare the spectral properties while keeping the surface state of the nanoclusters unchanged.[13,14] In the present work, we have studied the PAS of a series of different average grain sized nanoclusters of ZrO_2.

II. EXPERIMENT

The ZrO_2 nanoclusters of an average diameter of about 5 nm have been prepared by the hydrothermal method. A solution of 1-N zirconium nitrate in 2-N nitric acid is heated to 150 °C for 12 h in a sealed hyperbaric vessel cushioned with polytetrafluoroethylene, and is then naturally cooled to room temperature. The product is washed repeatedly with water and absolute acetone alternately and the white nanoclusters of ZrO_2 are obtained. These are dried in a vacuum desiccator for 14 h and are then stored in a desiccator. By annealing them at different temperatures for 8 h, nanoclusters of different size are obtained. The temperatures chosen are 300 °C, 500 °C, and 900 °C. The average diameters of the ZrO_2 nanoclusters have been measured using the H-900 TEM and D/MAX-r rotation anode x-ray diffractometer. X-ray diffraction spectra have been measured for four samples and all peaks can be indexed according to the standard monoclinic structure following Cohen's method. The photoacoustic spectroscopy system consists of a xenon lamp source, a monochromator, a chopper, photoacoustic cells, a lock-in amplifier, and a computer. For our measurements, the chopper frequency is 30 Hz, the scanning velocity is 1.03 nm/s, and the wavelength range is 350–600 nm (there is no absorption peak or edge in the wavelength range of 600–800 nm). The measurements are controlled and monitored by the computer automatically. All the data have very good reproducibility. The photoacoustic signal with respect to the frequency is measured. The light source is a HeNe laser ($\lambda = 6328$ Å) and the chopper frequency range is 30–186 Hz. The time constant of the lock-in amplifier is 1 ms. The thickness of the sample is about 1.7–1.9 mm.

III. RESULTS AND DISCUSSIONS

The ZrO_2 nanoclusters obtained are found to be nearly spherical with a diameter of 5 nm when studied with the TEM [see Fig. 1(a)]. The distribution of the diameters of the ZrO_2 nanoclusters is shown in Fig. 1(b). In Fig. 2, we have shown the variation of the grain size with annealing temperature. We know that the annealing of the samples goes through three steps, namely, the removal of the internal stress, the interface structure relaxation (or rearrangement of surface and interface atoms), and the growth of the grains. It is generally believed that the energy for the interface structure relaxation is smaller than that for the growth of the grains. Therefore, at lower temperatures ($T < 800$ K), the removal of the internal stress and the interface structure relaxation predominate, so the grain size increases slowly with the annealing temperature. On the other hand, at higher temperatures ($T > 800$ K), the growth of the grains predominates, so the grain size increases quickly with the annealing temperature. Figure 3 shows the PAS and first-order differential PAS of the ZrO_2 nanoclusters of different average size. From the PAS, we can see that the absorption edge is blueshifted as the average size decreases. From the first-order differential PAS, we can easily observe that the positions of the principal absorption peaks are 377, 385, 386, and 386.8 nm for the 5-, 10-, 15-, and 90-nm ZrO_2 nanoclusters, respectively.

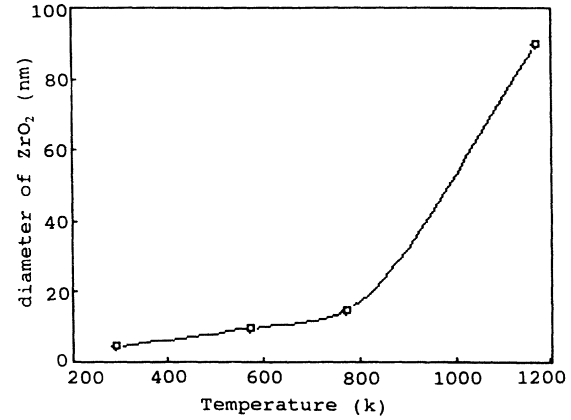

FIG. 2. The variation of the grain size with the annealing temperature.

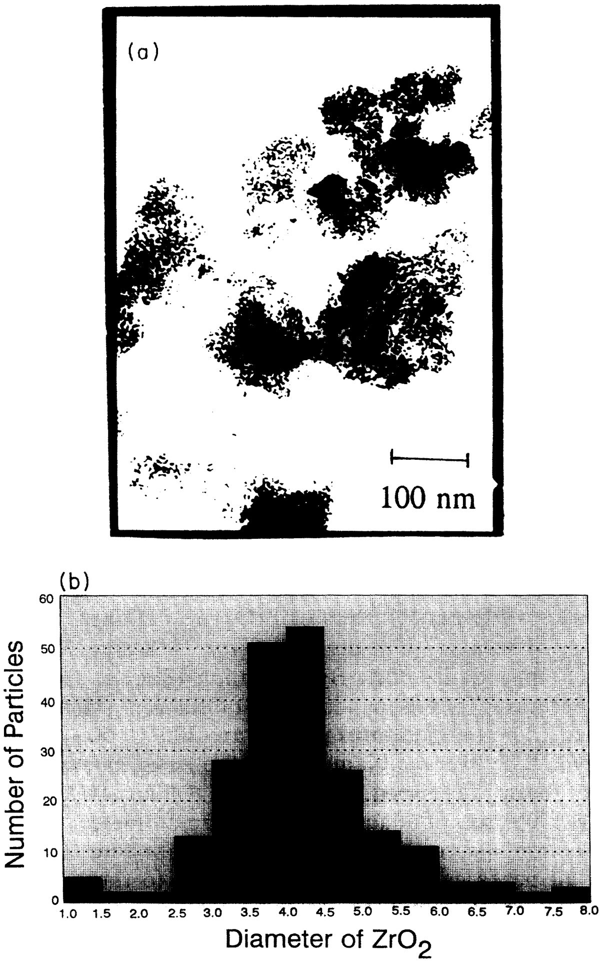

FIG. 1. (a) TEM micrograph of 5-nm diameter ZrO_2 nanoclusters. (b) The distribution of the diameters of the ZrO_2 nanoclusters.

If we consider the nanoclusters as spheroids, the lowest-energy state of the ZrO_2 nanoclusters can be analytically expressed as[10–12]

$$E = E_g + \frac{h^2\pi^2}{2R^2}\left[\frac{1}{m_e} + \frac{1}{m_h}\right] - 1.786\frac{e^2}{\varepsilon R} - 0.248 E^*_{\mathrm{Ry}} , \tag{1}$$

where R is the radius of the nanoclusters, ε is the dielectric constant, m_e and m_h are the effective masses of the electron and the hole, respectively, and E^*_{Ry} is the effective Rydberg energy. On the right-hand side of Eq. (1), the first term is the energy gap, the second is the quantum size localization energy, the third is the Coulomb interaction energy, and the fourth is a result of the spatial correlation effect, which is independent of the size and is usually small. By observing the signs of the terms, we see that the second term and the third term represent an increase and a decrease of energy, respectively. Since the quantum size localization energy of and the Coulomb effect are inversely proportional to R^2 and R, respectively, as the size of the nanoclusters decreases, the quantum size energy of localization will become significant. When it becomes greater than the Coulomb

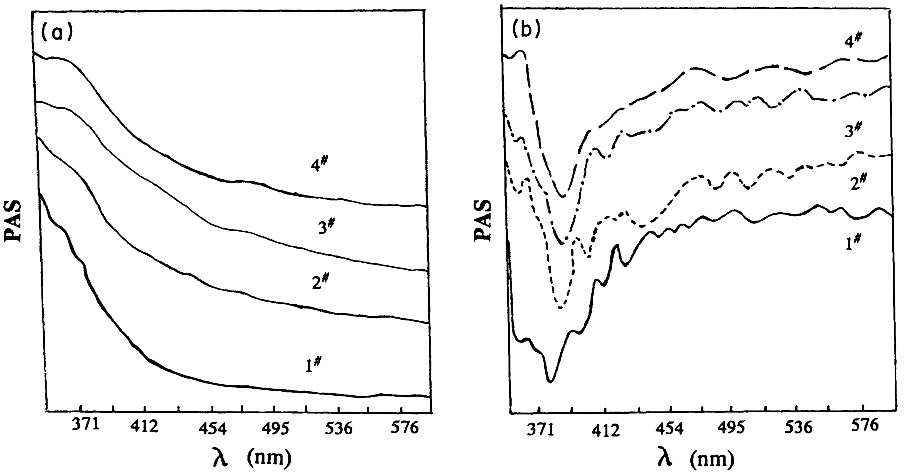

FIG. 3. The PAS (a) and the first-order differential PAS (b) of the ZrO_2 nanoclusters of different average size. #1: 5 nm; #2: 10 nm; #3: 15 nm; #4: 90 nm.

energy, the excitation energy increases and is higher than the eigenenergy state, which results in a blueshift of the absorption edge and the absorption peak. These are shown in Fig. 3.

From the PAS and the first-order differential PAS, we can also see that when the average size of the nanoclusters decreases to an extent such that it can be compared with the Bohr radius, the binding energy of the exciton increases. When a crystal absorbs a photon, it will excite an electron and a hole, and the electrostatic attraction will bound them to form an exciton. At this time, the significant increase in the quantum localization energy will result in the splitting of the energy band of the crystal. The Bohr radius of an exciton is[12,15]

$$r_a = \frac{h^2\varepsilon}{e^2}\left[\frac{1}{m_e}+\frac{1}{m_h}\right] . \tag{2}$$

Under normal circumstances where the binding energy is lower, the exciton can be excited by heating to form a free electron and a free hole, so the absorption of the exciton is not observed at room temperature.[16] However, when the diameter of the nanoclusters is smaller than 5 nm, due to the localization action of the exciton, the binding energy of the exciton will increase with the overlapping of space wave function of the electron and the hole and the coherent motion of the exciton. Therefore, the absorption of the exciton can be observed at room temperature. From the PAS shown in Fig. 3(a), we observe some small steps at the absorption edges. From the first-order differential PAS shown in Fig. 3(b), we see some split peaks which can be attributed to the exciton absorption of the ZrO_2 nanoclusters. When the size of the nanoclusters decreases, the absorption peak of the first-order differential PAS will widen and the relative absorption intensity in the longer-wavelength region will decrease. These can be attributed to the surface effect and the interaction between the nanoclusters. As the diameter of the nanoclusters decreases, their surface areas increase so the number of atoms and molecules at the surface increase. As a result, the disorder and the asymmetry in the crystal grows.

Figure 4 shows the variation of the PAS signal with the frequency and the variation of the thermal constants with the diameter of the ZrO_2 nanoclusters. The ZrO_2 samples have thermal diffusion lengths of approximately 10^{-5} m (corresponding to the frequency range between 10–100 Hz) and are thermally thin samples. In the present work, the optical-absorption length is smaller than the thermal diffusion length and the thickness of the sample, and the thermal diffusion length is smaller than the thickness of

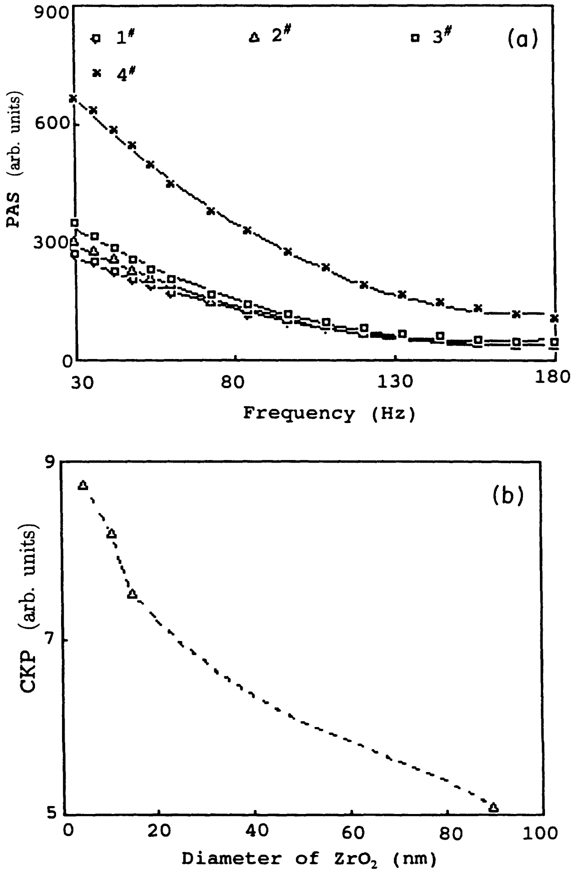

FIG. 4. (a) The variation of the PAS signal with the frequency. (b) The variation of the thermal constants with the diameter of the ZrO_2 nanoclusters.

the sample. The wavelength of the light source is 6328 Å and there is no absorption peak or edge in this wave band. According to the R-G theory, the photoacoustic signal Q can be approximately expressed as

$$Q = BF^{-1}(\rho\kappa C)^{-0.5}, \tag{3}$$

where B is a constant depending on the experimental equipment and conditions, F is the chopper frequency, ρ is the density of the sample, C is the specific-heat capacity, and κ is the heat capacity of ZrO_2. From Eq. (3), we can see that the product of the thermal constants $(\rho\kappa C)$ is inversely proportional to Q^2. When the product increases, the photoacoustic signal decreases rapidly. Figure 4(b) shows the rapid increase of the product with the decreasing diameter of ZrO_2 nanoclusters. As the number of atoms and molecules in the surface or near the surface increases, the interaction between surface atoms and surface atoms in the medium nearby and neighbor clusters increases. The motion due to heating for the surface atoms are more violent than that for interior atoms. As a result, the specific-heat capacity and the thermal conductivity of the ZrO_2 nanoclusters will increase.

In this study, we can see that the PAS technique can directly measure and compare the spectral properties and thermal properties while keeping the surface state of nanocluster or nanostructures unchanged. With a decrease of the average size of the nanoclusters of ZrO_2, we have observed a blueshift of the cutoff wavelength of the PAS absorption edge and the peak of the first-order differential spectrum, the emergence of fine structures of the absorption edge, a broadening of the peak, and a significant increase in the thermal constant of the nanoclusters, etc. These phenomena are related to the quantum size effect, the interaction of nanoclusters, the super surface effect, and the microstructure of ZrO_2. These show that nanostructural oxides offer the possibility of changing the bulk structure on the molecular level, and give rise to a variety of interesting physical properties. Moreover, people can create a variety of ultrafine ceramics and new nanostructural compound materials of metals and nanostructural oxides, with different sizes and specific functions. In conclusion, these materials present new physics and chemistry, and have very good prospects for having a wide range of applications.

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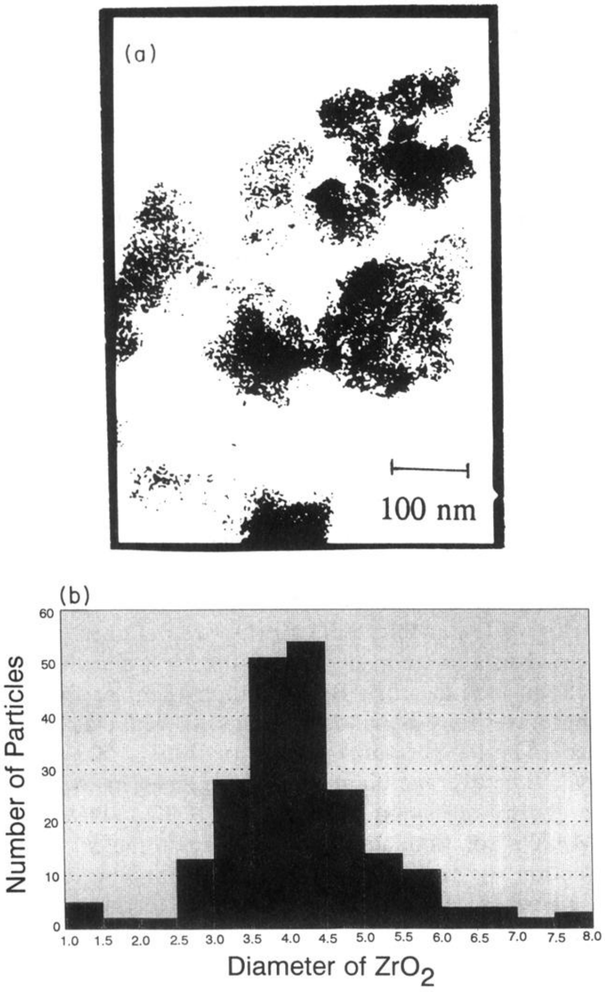

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