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Enhanced Raman scattering from nano-SnO_2 grains*

Ding Shuo(丁 硕), Liu Jin-Quan(刘金全), and Liu Yu-Long(刘玉龙)†

Institute of Physics, Chinese Academy of Sciences, Beijing 100080, *China*

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We present the Raman spectra of nano-SnO_2 grains with sizes from 4nm to 80nm excited by 532nm and 1.06μm lines. The enhanced Raman scattering of the nanograins is observed for both exciting lines when the grain size is less than 8nm. The less the grain size is, the more intensely the Raman scattering is enhanced. According to our results, the enhancements of the Raman intensity are a few tenfolds and different for different exciting lines when the grain size is 4nm. It can be attributed to enhanced Raman scattering by electron–hole pair excitations in the nanograins that originate from sub-microscopic (10nm) size and other defect- and surface-related features. A critical size that divides respective predominance of bulk properties and the defect-, surface-, and size-related features can be determined to be about 8nm.

Keywords: nano-SnO_2 grains, enhanced Raman scattering, electron-hole pair
PACC: 3320, 6146

Tin oxide (SnO_2) has excellent photoelectronic properties and sensitivities to gases, and has attracted much attention in the past because of its potential applications in various areas of physics and chemistry.[1−4] Nano-SnO_2 possesses some different characteristics from the crystalline form[5,6] and has found applications in gas sensor technology.[7] Some earlier work on Raman scattering in nano-SnO_2 studied its Raman-active vibration modes and some related micro-structural changes of grains and the change of space symmetry with the annealing temperature.[8] However, the intensity of the Raman spectra of nano-SnO_2 grains is never touched upon.

There have been a few investigations that concentrate on the enhancement of the Raman intensity of microstructures around a few hundred nanometres.[9] To our knowledge, however, the enhanced Raman scattering of nanograins around a few nanometres has not been reported.

In this paper, we study the intensity of nano-SnO_2 grains. We present the Raman spectra excited by 532nm and 1.06μm of nano-SnO_2 grains with different annealing temperature. The enhanced Raman scattering of nanograins is observed and explained.

The nano-SnO_2 grains with an average grain diameter smaller than 4nm were obtained by the hydrothermal method.[8] Sample pieces for measurements were prepared by pressing the powder at a pressure of 200Mpa. Isothermal annealing at 200, 400, 800 and 1000°C for 6 hours yielded samples with average grain sizes of 4, 8, 40 and 80nm respectively, as determined by both TEM micrograph and the XRD Scherrer formula.[8] Two Raman spectrometers were used for investigating the vibration modes of nano-SnO_2 grains at room temperature. One was a SPEX-1403 Raman spectrometer together with a Coherent DPSS 532-200 laser for 532nm excitation. Another was a Bruker 100 system, a near-infrared Fourier transform Raman spectrometer (FT-RS) with a cw diode-pumped Nd:YIG laser for 1.06μm excitation. Backscattering geometry was adopted for all Raman measurements. In general, Raman spectra were collected under the conditions of laser power 50mw and resolution 2cm^{-1}. For these two systems, we obtained the Raman spectra of the samples under the uniform condition respectively.

Figures 1 and 2 show the FT–Raman spectra of nano-SnO_2 grains and the Raman spectra of nano-SnO_2 grains excited by 532nm, respectively. All curves are plotted on the same scale in these two figures. In Figs.1 and 2, B_1 and B_2 peaks are attributed to the surface phonon modes, and A_1, A_2 and A_3 peaks are explained by the interior phonon modes of the crystal.[8]

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†E-mail: ylliu@aphy.iphy.ac.cn

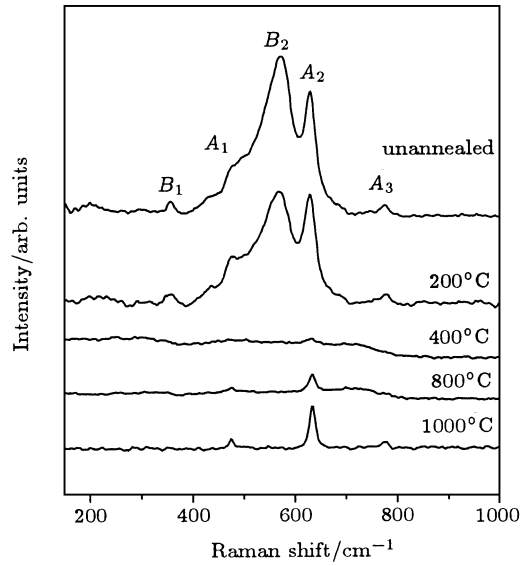


Fig.1. FT–Raman spectra at room temperature of nano-SnO_2 grains with different annealing temperatures.

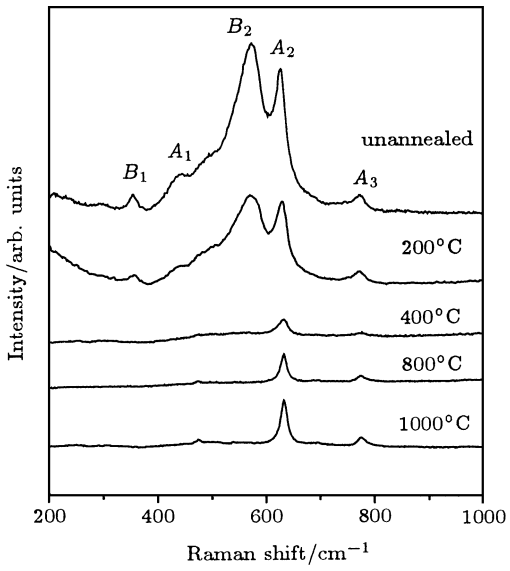


Fig.2. Raman spectra at room temperature of nano-SnO_2 grains with different annealing temperatures excited by 532nm.

Because A_2 peak is strong and easy to resolve accurately, we give the relationship between the integral intensity of A_2 peak and crystal size in Fig.3. The intensity of 80nm grains excited by different lines is plotted as the same magnitude in the graph for the sake of comparison. With the decrease of the grain size, the intensity of the bulk modes lowers and reaches a minimum at 8nm; however, the intensity goes up again at smaller sizes than 8nm. The difference between 532nm excitation and 1.06μm excitation is that the intensity excited by the former is enhanced more strongly at 4nm.

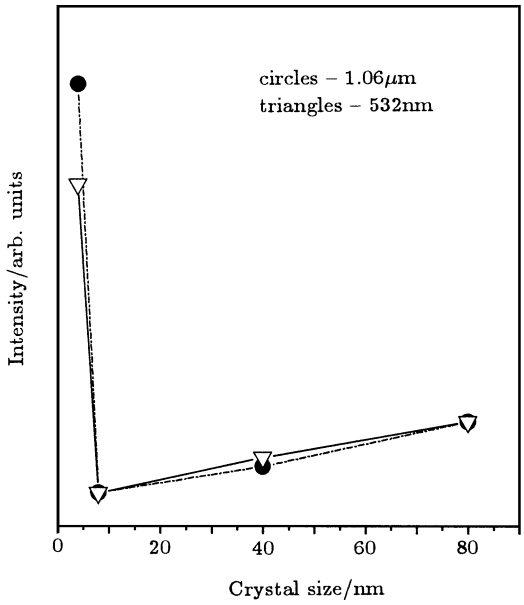


Fig.3. Plot of the integral intensity of A_2 peak as a function of the nano-SnO_2 grains size. Triangles: excited by 532nm; circles: excited by 1.06μm.

The intensity of Raman scattering is proportional to the atoms involved, so the normal relationship between the intensity of the bulk modes and crystal size is similar to that between the ratio of bulk atoms (N_B) to total atoms (N_T) and crystal size shown in Fig.4.[10] In fact, it has been reported that the bulk modes decrease and disappear when the grain sizes become less and less.[11,12] The similarity is also substantiated in Fig.3 when we only check the curve ranging from 8nm to 80nm for both 532nm and 1.06μm exciting lines. We fit the normal intensity of 4nm grains using the data from 8nm to 80nm according to the trend in

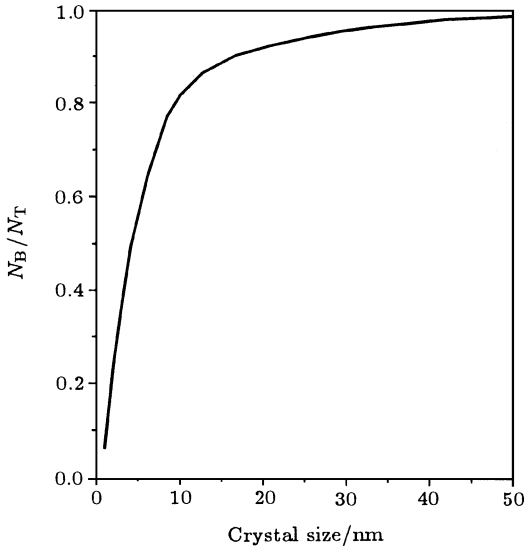


Fig.4. The relationship between the ratio of bulk atoms (N_B) to total atoms (N_T) and crystal size.

Fig.4 and find that the enhancement factors are 12 for 532nm and 26 for 1.06μm. Considering that nanograins of smaller size have less density, the real enhancement factors are larger.

Although we select the intensity of A_2 peak to examine, other peaks are also enhanced identically.

Unlike other microstructures reported in other articles about the enhanced Raman scattering,[9] the size of the nanograins here is not comparable to but far less than the wavelength of exciting line. Similarly, the electromagnetic mechanism of enhancement is no longer applicable. The unusual Raman scattering enhancement can be attributed to enhanced Raman scattering by electron–hole pair excitations in the nanometre grains that originate from sub-microscopic (10nm) size[13] and other defect- and surface-related features. Sub-microscopic size causes the breakdown in the conservation of momentum, which is due mainly to the enhanced electron–hole excitation. The enhanced excited free carriers couple with the particle lattice to induce the unusual Raman scattering enhancement. At the same time, the size of several nanometres is comparable to the penetration of the electron–hole wavefunctions, which is useful for interaction between different nanograins. Its specific mechanism has been proposed in other articles about the surface enhanced Raman scattering.[13] The reason why longer wavelength is more advantageous to the enhancement is perhaps that the electron–hole pair excitation is more efficient and more sensitive to a longer exciting line.

In addition, although the intensity of the as-grown grains is enhanced and the size is the same as the 4nm sample after 200°C annealing, the intensity is a little less than that of the sample after annealing. This indicates that annealing leads to a relaxation in the interface structure and makes the lattice of the grains more regular.

In summary, the Raman spectra of nano-SnO_2 grains with sizes from 4 nm to 80 nm were excited by 532 nm and 1.06 μm lines. The enhanced Raman scattering of the nanograins is observed for both exciting lines when the grain size is less than 8 nm. The smaller the grain size is, the more intensely the Raman scattering is enhanced. According to our results, the enhancements of the Raman intensity are a few tenfolds and different for different exciting lines when the grain size is 4nm. This can be attributed to enhanced Raman scattering by electron–hole pair excitations in the nanograins that originate from sub-microscopic (10 nm) size and other defect- and surface-related features. Considering the changes of the XRD spectra and the lattice parameters, the appearance of the surface modes[8] and the changes of Raman scattering intensity, a critical size that divides respective predominance of bulk properties and the defect-, surface-, and size-related features can be determined to be about 8nm.

References

[1] Miyasaka T 1979 *Nature* **277** 638

[2] Ogawa H 1981 *J. Electrochem. Soc.* **128** 2020

[3] Kang J Y 2001 *Acta Phys. Sin.* **50** 2198 (in Chinese)

[4] Smay G L and Wasylyk J S 1981 *Glass Technol.* **22** 2516

[5] Ishida T 1994 *J. Electrochem. Soc.* **141** 1357

[6] Bedja I, Hotchandani S, Carpentier R, Fessenden R and Kamat P 1994 *J. Appl. Phys.* **75** 5444

[7] Gopel W and Reinhardt G 1996 *Sensor Update* **1** 12

[8] Yu K N, Xiong Y H, Liu Y L and Xiong C S 1997 *Phys. Rev.* B **55** 2666

[9] Murphy D V and Brueck S R J 1983 *Opt. Lett.* **8** 494

[10] Feng D, Wang Y N and Qiu D R 1989 *Metallphysics* (Beijing: Science Publishing House) p408 (in Chinese)

[11] Chuu D S, Dai C M, Hsieh W F and Tsai C T 1991 *J. Appl. Phys.* **69** 8402

[12] Hayashi S and Yamamoto K 1986 *Superlattices Microstruct.* **2** 581

[13] Burstein E, Chen Y J, Lundquist S and Tosatti E 1997 *Solid State Commun.* **29** 567