Microstructure of SnO_2

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The microstructure of SnO_2 prepared by the sol-gel method, was studied by scanning electron microscopy, transmission electron microscopy, high-resolution electron microscopy, and x-ray diffraction. A nanosponge structure was observed. There is much surface and interface structure. The interfaces vary in type from amorphous to crystalline. The high-density of defects greatly influences the physical and chemical properties of this material.

I. INTRODUCTION

SnO_2 is a kind of wide energy gap *n*-type semiconductor. The existence of a donor point defect causes the conductivity of the material. In recent years, SnO_2 have extensive applications in sun-energy battery, catalyst,[1] gas sensor material,[2] transparent electrode material, etc. Many studies of the electrical properties of SnO_2 have been reported.[3–6] The electrical properties indicated are strongly dependent on the structure of SnO_2.[7] However, only its microstructure in μm scale had been studied. The purpose of the present work is to study the microstructure in nm scale by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and high-resolution electron microscopy (HREM). These methods provide more detailed information of the microstructure.

II. SAMPLE AND PREPARATION

$SnCl_4 \cdot 5H_2O$ (analysis pure grade) was dissolved in distilled water. A certain amount of ammonia was used to adjust the pH of the solution to 6. The solution was heated to 80 °C, then generating a milky-white SnO_2 gel. The reaction equation is

$$SnCl_4 + 4NH_4OH \xrightarrow[\Delta]{H_2O} SnO_2\downarrow + 4NH_4Cl .$$

The gel was washed with distilled water to remove Cl^- and NH_4^+ ions, and then dried at different temperatures (80°, 150°, 250°, or 400 °C), and a pale yellow colored dry gel was formed.

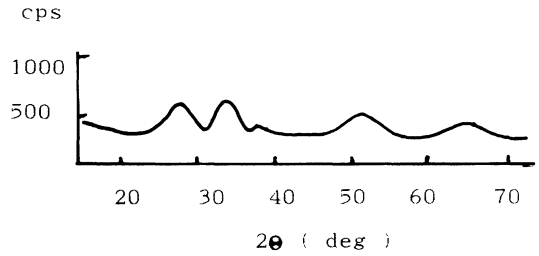

FIG. 1. X-ray diffraction spectrum of dry gel SnO_2.

Figure 1 is a typical x-ray diffraction spectrum of the dry gel powder of SnO_2. The experiment was conducted on a Geigrerflex D/MAX-rA rotating x-ray diffraction spectroscopy with a copper target at an operating voltage of 40 kV and an electric current of 100 mA.

In the spectrum, four broad diffraction bands can be found. The peak positions of these bands are 26.9°, 33.6°, 51.8°, and 64.2°. They correspond to the lattice spacings of tetragonal SnO_2:$d[110]=0.33166$ nm, $d[101]=0.26671$ nm, $d[211]=0.17648$ nm, and $d[112]=0.14506$ nm for gel dried at 80 °C. The peak half height breadths are 4.2°, 4°, and 4.6°.

According to the Scherrer formula

$$L_{hkl}=\frac{K\lambda}{\beta_{hkl}\cos\theta_{hkl}} ,$$

where λ is the wavelength of the x ray, β_{hkl} is the half height breadth of the $[hkl]$ diffraction peak, θ_{hkl} is the diffraction angle, L_{hkl} is the length of crystal in the (hkl)

FIG. 2. The SEM morphology of dry gel SnO_2, enlarged 2000 times.

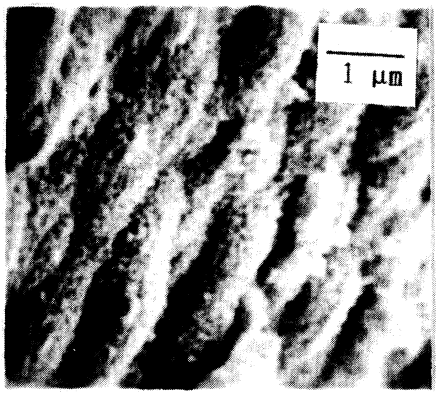

FIG. 4. The SEM morphology of dry gel SnO_2, enlarged 10 000 times.

direction, and $K=0.9$.

The length of the crystal in the (110) direction is $L_{110}=1.944$ nm. The product is nanometer crystallite materials. The crystallite size is about 2 nm.

When the product was dried at higher temperatures, the crystallite size became larger. At 400 °C the crystallite size is about 5 nm.

III. OBSERVATIONS OF ELECTRON MICROSCOPE

SEM measurement was conducted on an X-650 scanning electron microscope, TEM measurement was conducted on an H-800 transmission electron microscope, HREM measurements were performed on an electron 200 CX and JEOL 4000 EX high-resolution electron microscope.

Figures 2, 3, and 4 are some morphologies of dry gel SnO_2 particles enlarged in different times with SEM. Figure 2 shows that the cross section of the dry gel is like a sell bulk cross section, not an agglomerate of powders. Figures 3 and 4 show the porous microstructure of the surface of the gel particle.

Figure 5 is the TEM morphology of the dry gel SnO_2, which was ground in a mortar and then ultrasonically separated in alcohol for 30 min. There are many grains and holes about 5 nm in size. The electron diffraction pattern of the selected area (Fig. 6) appeared to be typical polycrystalline diffraction rings. According to the diameters of the rings, the spacings are 0.33, 0.27, and 0.18 nm, respectively. They are in accordance with the spacings of [110], [101], and [211] of tetragonal phase SnO_2. This indicates that the gel is nanocrystalline tetragonal SnO_2.

Figure 7 is a HREM image of the gel. The gel bulk was ground into powder then compacted in 1 GPa, ground again and ultrasonically separated in alcohol for 30 min for observation. Many crystals of about 5 nm with clear lattice strings can be seen. The connected crystals form a random network, in which are many various nano-sized holes. We call this structure a "nanosponge structure." This microstructure leads to a very high rate of interface and surface.

There are a lot of nanometer grains in Fig. 8. Most lattice images in these interfaces are clear enough. This demonstrates that there are no disorder areas in these interfaces. However, nano-sized amorphous areas can sometimes be found in the interfaces (Fig. 9). Some interfaces are between above mentioned two: some interfaces are with some width, the lattices in these interfaces are somewhat distorted, but not totally disordered. They are like the interfaces in conventional polycrystalline materials, but with high rate. The interfaces are rough or smooth according to the circumference condition. Usual-

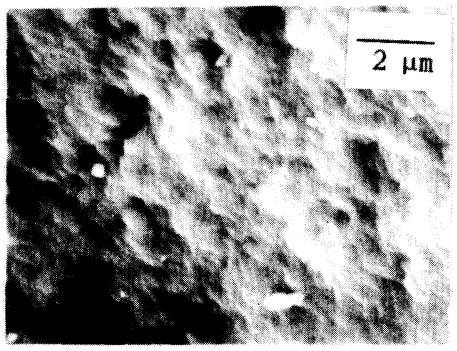

FIG. 3. The SEM morphology of dry gel SnO_2, enlarged 5000 times.

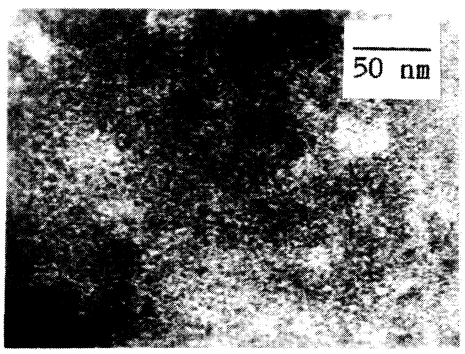

FIG. 5. The TEM morphology of dry gel SnO_2, enlarged 200 000 times.

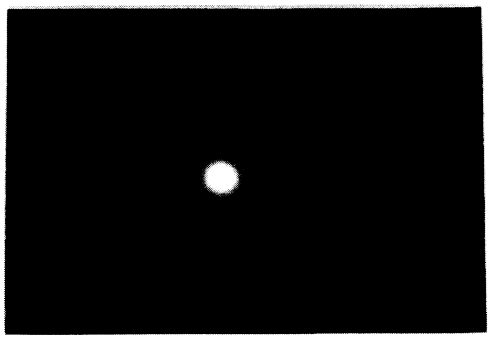

FIG. 6. The select area electron diffraction of Fig. 5.

ly the interface between nanocrystals is smooth, and the interface between the nanocrystal and amorphous area is rough.

A twin-crystal grain is shown in Fig. 9. The grain has very good symmetry with the interface. The interface is very perfect. The grain is generated through the symmetrical face of the twin crystal. The forefront of growth of grain is the lower part of the grain. The growth of the [110] face and the down growth of the twin-crystal face wholly controlled the growth process of the grain. This caused the good symmetry of the grain. The down part under the twin crystal was an amorphous region that supplied materials for the down growth of the grain. This interface, or front edge of the twin crystal, is rough. Two crystals connected with a little angle crystalline boundary can be seen in the left of the twin crystal. The width of the boundary is about 5 or 6 layers of lattice face. The symmetry of this grain is poor. These two crystals were generated separately. When they grew up, they met and formed this boundary.

The upper right side of Fig. 9 is a flowerlike polycrystal. In the grain, six crystals of different lattice direction compacted together, but the integer of every grain is not so good that many seriously distorted lattices can be seen. In most grains in all of the above HREM photos, many crystalline lattice distortions can be found, as well as some dislocations, little angle boundaries, and stacking faults.

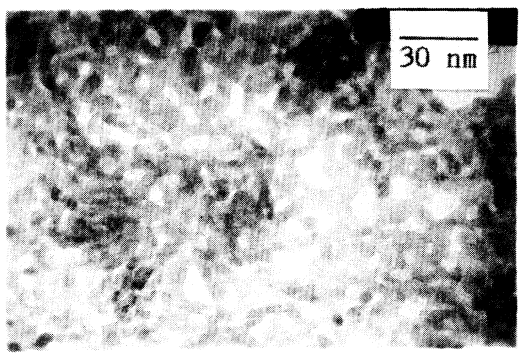

FIG. 7. The HREM morphology of dry gel SnO_2, enlarged 360 000 times.

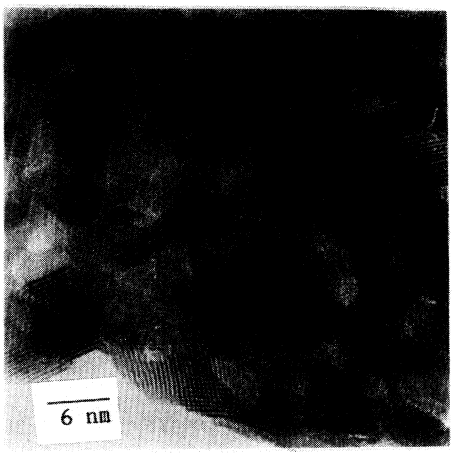

FIG. 8. The HREM morphology of dry gel SnO_2, enlarged 3600 000 times.

All of these results demonstrated that the "gaslike interface model," which was suggested by H. Gleiter,[8] is not suitable for nano SnO_2. The "gaslike interface model" means that the atom distribution in the interface is like the atom distribution of gas, without any long-range or short-range order. However, in our observations of many interfaces of nano SnO_2, the lattice fringes are clear enough. The interfacial structure is more ordered than "gaslike" and to have some short-range order.

The surfaces of the grains are between grains and holes. They are usually smooth but not flat. This indicated that the network structure is formed before forming crystalline grains at low temperatures. The total area of surface per cm^3 can be estimated as follows: if the hole is a sphere of radius r, the number of holes in a bulk of 1 cm^3 is N, the total surface of these holes in 1 cm^3 is S,

$$S = N4\Pi r^2 = \frac{3}{r}(N\tfrac{4}{3}\Pi r^3) = 3\frac{V}{r} ,$$

where V is the total volume of holes, which can be measured by the specific gravity of the sample. S is the directly proportional to the volume of holes, and inverse-

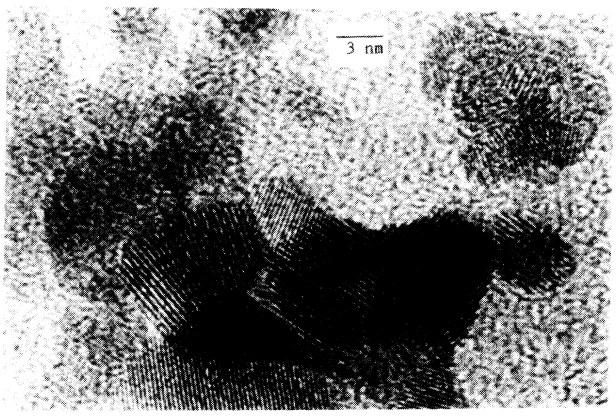

FIG. 9. The HREM morphology of dry gel SnO_2, enlarged 3800 000 times.

ly proportional to the size of the hole. The nanometer holes cause a very large surface area and many dangling bonds, which usually connected to other molecules such as H_2O, O_2, Cl_2, etc. This microstructure feature introduces high chemical activity and absorptivity. Meanwhile, the depth of the surface is on the same order as the size of the crystalline grain. This must make the surface states of electrons and phonons of nanocrystallites different from that of conventional polycrystallite. Usually the phonon is softened, the energy levels of the electron are separated.

SUMMARY

Electron microscopic research indicates that nano-SnO_2, prepared by the sol-gel method, is a kind of nanosponge structure. It is a kind of porous bulk material, consisting of many evenly distributed nanometer-sized holes and many nanocrystals. The nanocrystals (and/or amorphous particle) connect to each other into a random network. This microstructure leads to a very high rate of surfaces and interfaces. Many interfaces are perfect. Some are distorted. Still some distorted lattices, dislocation, little angle boundaries, and stacking faults exist in the grains and interfaces. The interface structure is very disordered but not "gaslike." Most of these defects are somewhat like those of conventional polycrystalline materials, but with a very high rate. There are a very large amount of surface structures, and the same volume of the interface structure. The depths of these surfaces are of the same order with the size of the grains. This is a very important difference from conventional polycrystals. Inside some grains, many distorted lattices can be found. This is rare in conventional materials. They are the characteristics of microstructure of nano-SnO_2—a high defect density structure. This structure is very helpful for catalysis, sensibility of electrical conductivity for gas and pressure. The further work is being undertaken in detail.

ACKNOWLEDGMENTS

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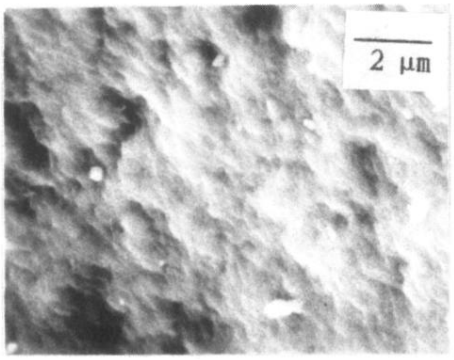

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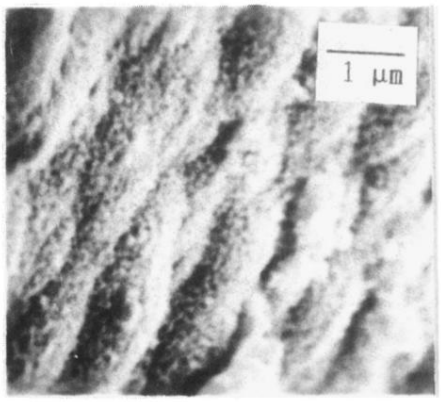

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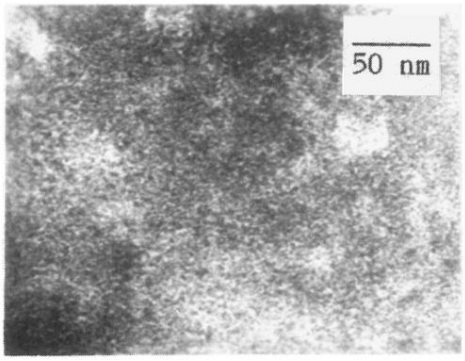

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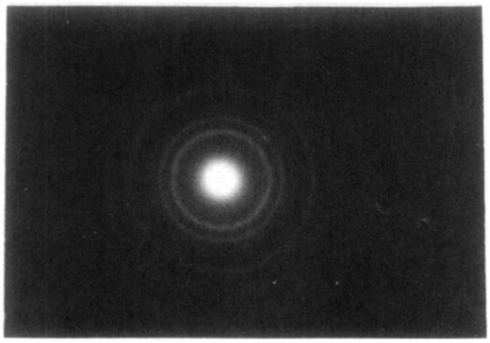

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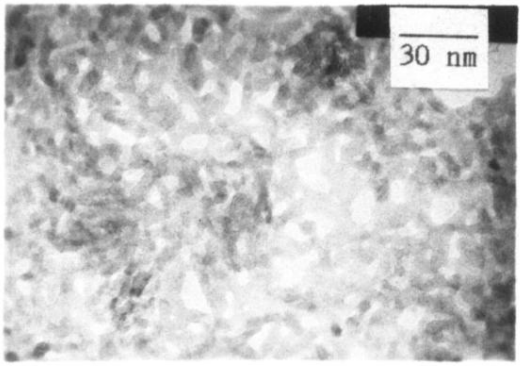

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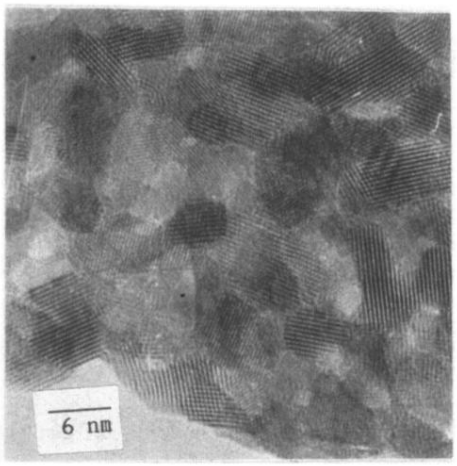

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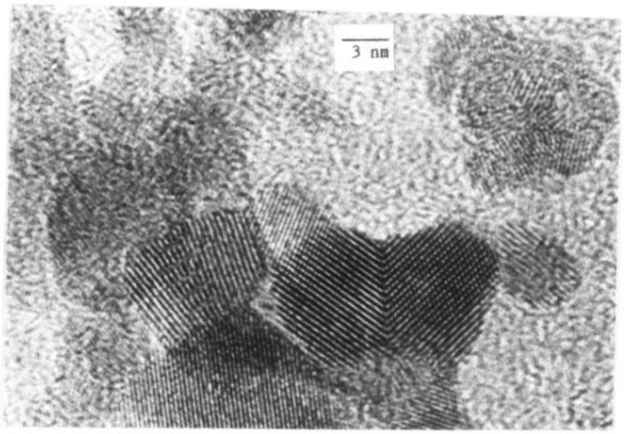

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