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TEM Observation of the Dispersion State of Pd on SnO_2

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High resolution transmission electron microscopy revealed finely dispersed Pd particles on SnO_2 crystallites. Pd particle size distributions as well as other related parameters were elucidated as a function of Pd loading. It was also suggested that PdO particles had greater affinity to the SnO_2 surface than Pd.

Semiconductor gas sensors are usually added with a small amount of noble metals such as Pd and Pt as a promoter for gas sensing.[1-2] The promoting effect of these additives is deeply related with their activities to oxidize inflammable gases. Generally, the effect strongly depends on the kind and loading of the added metal. In the case of SnO_2-based sensors, Pd is exclusively loaded by less than 1 wt%, and an excessive loading is known to lead to total loss of promoting effects. As already pointed out, the promoting effect of noble metals possibly arises through two sensitization mechanisms, chemical and electronic.[3-5] The chemical sensitization is mediated by activation of inflammable gases on the noble metal followed by spilling-over to the semiconductor surface. By contrast, the electronic sensitization is mediated by the direct exchange of electrons between the noble metal and the semiconductor surface: Inflammable gases interact with the noble metal to change its oxidation state which in turn causes a change in conductivity of the semiconductor. These arguments, however, still remain considerably speculative even for the most popular gas sensor system of Pd-SnO_2 because of a lack of definite information on the dispersion state of Pd. Direct observation of Pd-SnO_2 system by using a transmission electron microscope (TEM) has not been so successful because the atomic numbers of Pd (Z=46) and Sn (Z=50) are too close to each other to give a high contrast image of Pd particles in the usual samples. After several attempts, we found that a sufficiently high contrast image of Pd particles could be obtained by using the base particles of SnO_2 calcined at an unusually high temperature of 900 °C. Thus we have succeeded for the first time in elucidating the dispersion state of Pd on SnO_2, as stated below.

To prepare SnO_2 powder, stannic acid precipitated from an aqueous $SnCl_4$ solution with ammonia was washed thoroughly with deionized water, dried at 100 °C, and calcined at 900 °C for 2 h in air (specific surface area 7.3 m^2/g). Pd loaded samples were prepared by impregnating the above powder with a dilute sulfuric acid solution of $PdCl_2$, followed by evaporation to dryness and reduction in a flow of H_2 at 300 °C for 3 h. Pd loadings were set to 0.3, 1.0, 3.0, and 5.0% in weight of the prepared samples. TEM observation was carried out on a high resolution

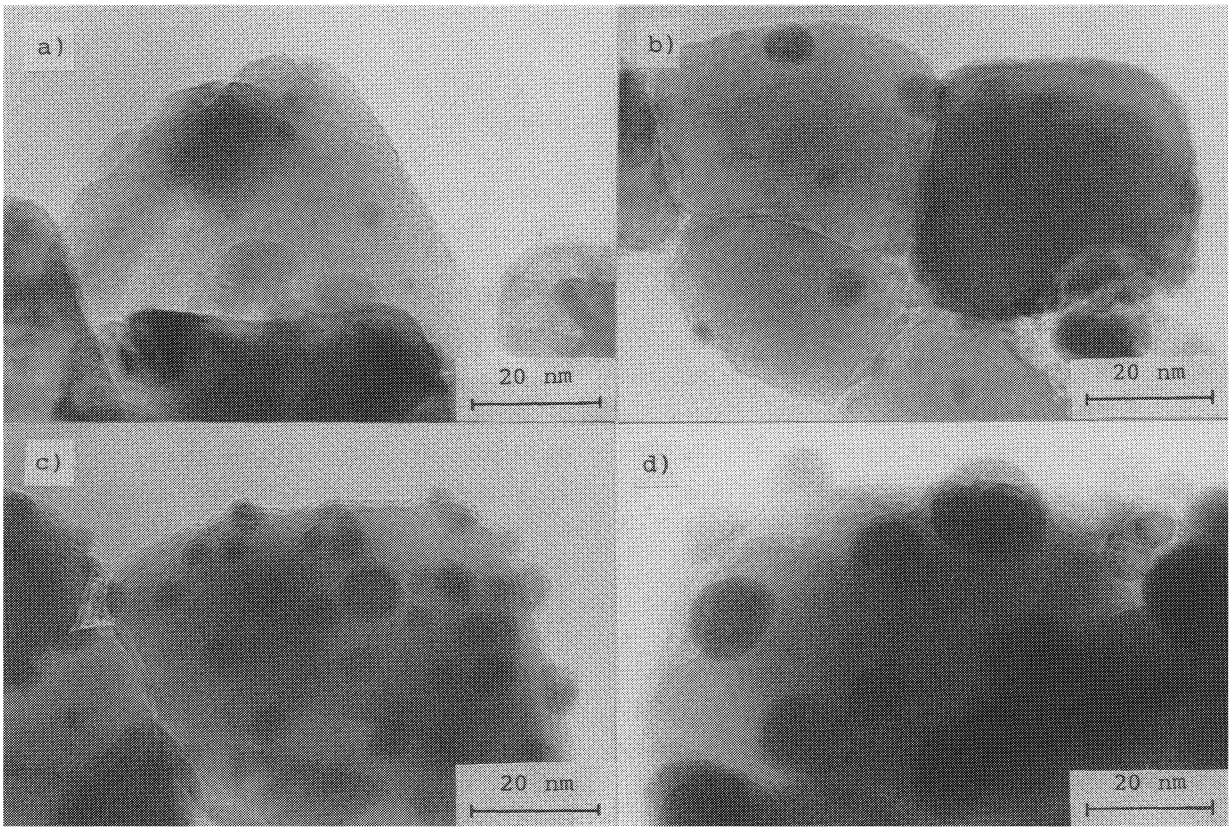

Fig. 1. TEM photographs of Pd particles dispersed on SnO_2 crystallites.
a) 0.3 wt%, b) 1.0 wt%, c) 3.0 wt%, d) 5.0 wt%

electron microscope (JEOL 2000EX) by using a 200 keV electron beam. TEM specimens were prepared as follows. The above Pd-SnO_2 powder was sieved to collect particles under 235 mesh and a portion of the collected particles was dispersed in methyl alcohol under a supersonic vibration. A drop of the dilute suspension was taken on a collodion film, and dried on a filter paper and then by evacuation.

In our early attempts, Pd was loaded on SnO_2 powder calcined at 600 °C. The SnO_2 crystallites, having a size of ca. 15 nm in diameter, were heavily aggregated together to severely degrade the contrast image of Pd particles dispersed on them. By raising the calcination temperature to 900 °C, SnO_2 crystallites became nearly doubled in size (ca. 30 nm or above) and less aggregated together. Such crystallites gave a distinct image of Pd particles. Figure 1 shows TEM pictures of the dispersed Pd particles on SnO_2 after the reduction with H_2 at 300 °C. Each Pd particle was recognized clearly as a dark contrast being attached on the peripheries of SnO_2 crystallites. A separate experiment using an analytical electron microscope confirmed that the dark contrasts were in fact given by Pd particles. The size and number of Pd particles were seen to change significantly with a change in Pd loading.

The sizes of 100 to 150 Pd particles were measured on TEM pictures for each Pd

loading. Resulting particle size distributions for the four Pd loadings are shown in Fig. 2. At 0.3 wt% Pd, the 1.5-3 nm range was most densely populated in the histogram. With increasing the Pd loading to 1.0 and 3.0 wt%, the highest population shifted to the 4.5-6 nm range, while a further increase to 5.0 wt% resulted in a large shift of the highest population range as well as in a very broad particle size dispersion. Based on the above particle size distributions, the mean particle size (D) as well as the total surface area (S) of Pd per gram of sample were estimated. D was determined as $D = \Sigma D_i \cdot n_i / \Sigma n_i$, where n_i and D_i denote the number and mean size of the particles belonging to the i th range of the histograms, respectively. On assuming spherical Pd particles, S was calculated according to $S = (\Sigma 4\pi r_i^2 \cdot n_i)(W/d)/(\Sigma(4/3)\pi r_i^3 \cdot n_i)$, where r_i is equal to $D_i/2$, and W and d are weight and density of Pd metal, respectively. The results are shown in Fig. 3 together with the number of Pd particles (m) per fixed surface area (30 nm x 30 nm) of SnO_2 as counted on TEM pictures. As shown in Fig. 3, the mean particle size D increased gradually with increasing Pd loading up to 3.0 wt% but it suddenly increased enormously at 5.0 wt%. This behavior was well reflected on those of S and m, both of which had a maximum at maximum at 3 wt% Pd.

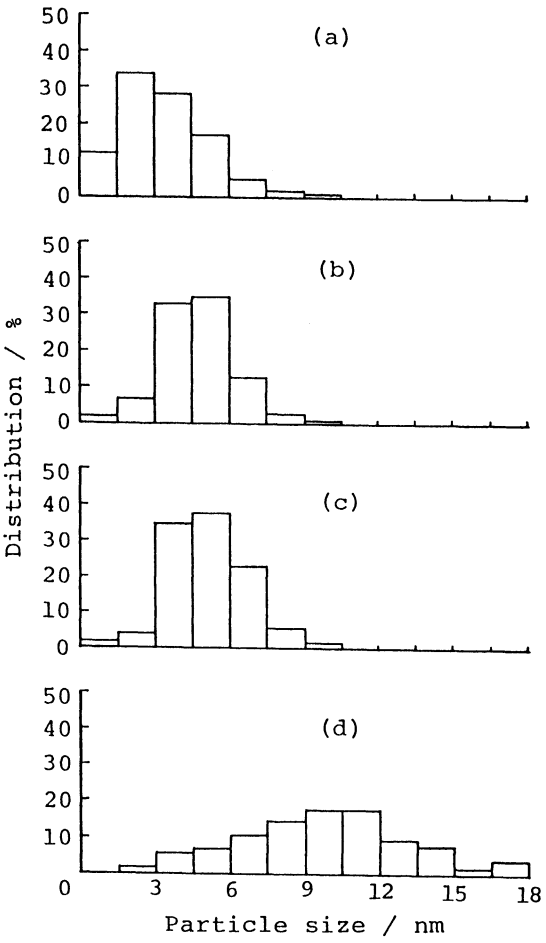

Fig. 2. Pd particle size distributions on SnO_2 crystallites based on TEM photographs.
a) 0.3 wt%, b) 1.0 wt%, c) 3.0 wt%, d) 5.0 wt%

From these observations, the features of the dispersed state of Pd on SnO_2 may be stated as follows.

1. Pd particles are finely dispersed at small Pd loadings, the mean sizes being well below 5 nm up to 1.0 wt%.
2. There is an optimum Pd loading which gives a maximum in the total surface area or surface density of Pd particles.
3. The distribution of Pd particles on SnO_2 is well uniform without showing any preference to particular locations such as necks and grain boundaries between SnO_2 crystallites.

The TEM observations mentioned above dealt with the dispersion of Pd after reduction with H_2. It is known that Pd is oxidized into PdO in an oxygen atmosphere. It was found that, when Pd-SnO_2 samples were treated with air at elevated temperatures above 300 °C, Pd particles on SnO_2 crystallites became less visible. This is considered to be in part due to the formation of PdO which, having a

smaller electron density than Pd, gives a lower contrast to SnO_2. However, a very important phenomenon seems to be also involved. That is, it is highly possible that Pd particles change their shape on the oxidation to PdO. For example, a TEM picture obtained after calcination in air at 600 °C is shown in Fig. 4. Compared with roughly spherical particles of Pd in Fig. 1, the oxidized particles (PdO) had more irregular shapes, closer to hemispheres. It is conceived that PdO has greater affinity to the SnO_2 surface than Pd and tend to have particle shapes which allow better larger contacts to SnO_2. In Pd-SnO_2 sensors, there is an optimum Pd loading with regard to the promoting effect as stated previously. It is possible to correlate this optimum with the maxima in the total surface area (S) or surface density (m) mentioned above. More plausibly, however, the promoting effect may be strongly related with the total surface area (S): only those particles with a sufficiently large total surface area are susceptible enough to exhibit changes in shape on exposure to inflammable gases.

In conclusion, the dispersion state of Pd on SnO_2 was elucidated by TEM. Such works would provide very basic information on the semiconductor gas sensors. Further studies are going on to correlate the gas sensitivity with the dispersion state of Pd.

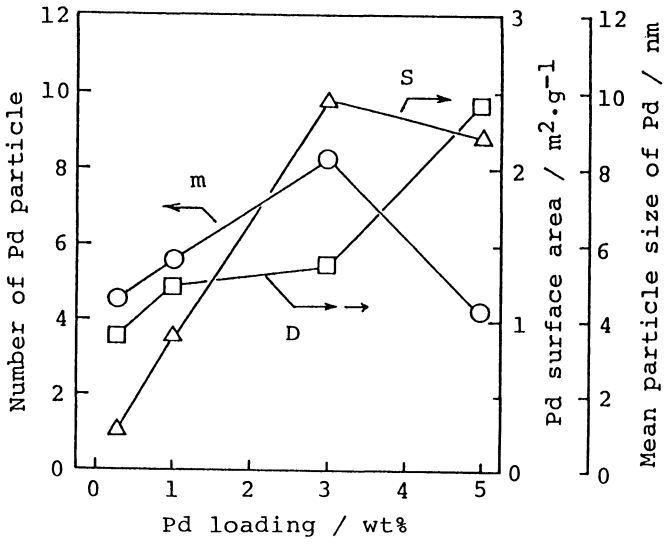

Fig. 3. Changes in the number of Pd particles per a fixed surface area (30 nm x 30 nm), the total Pd surface area per gram of sample, and the mean particle size of Pd with the Pd loading.

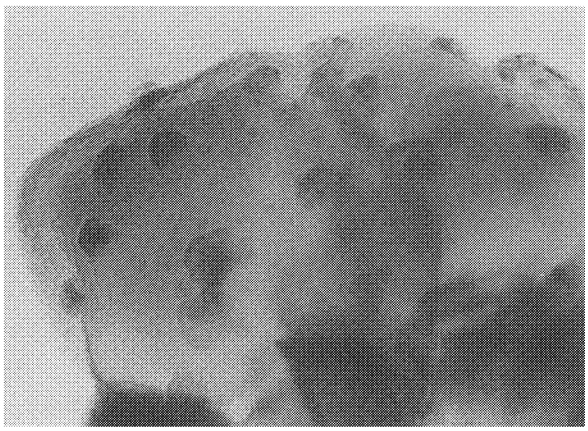

Fig. 4. TEM photograph of Pd particles dispersed on SnO_2 crystallites after oxygen treatment at 600 °C.

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